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REACTION OF IODINE CHLORIDE AND IODINE TRICHLORIDE WITH HYPOPHOSPHOROUS ACID

Ya. A. Fialkov and F. E. Kagan

As is well known, hypophosphorous acid can be classified as a fairly strong reducing agent.

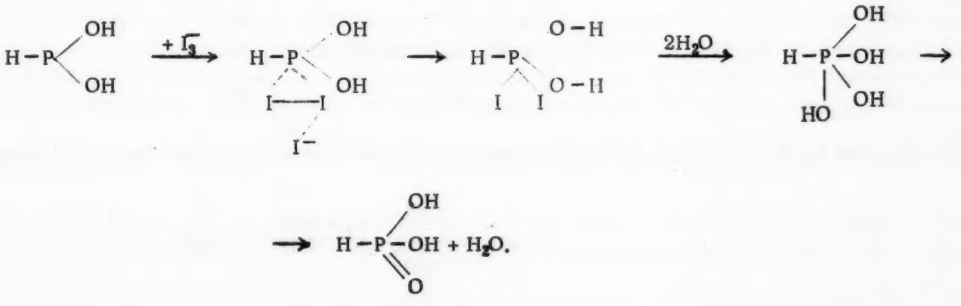
On the basis of the study of the oxidation reactions of hypophosphorous acid with various oxidizing agents, methods have been developed for the quantitative determination of hypophosphorous acid and its salts by the use of bromine [1], iodine [2], and potassium permanganate [3].

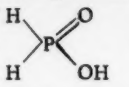
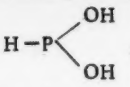
In the study of the oxidation mechanism of hypophosphorous acid attention has been directed to the unusual kinetics of its oxidation, namely, that at low oxidant concentration, the rate of oxidation of hypophosphorous acid by means of halogens, mercuric chloride and silver nitrate does not depend on the nature and the concentration of the oxidizing agent, but only on the proportional concentration of hydrogen ions [6].

The rate of oxidation of H_3PO_2 into H_3PO_3 is very low in alkaline medium but increases in proportion to the acidity of the solution. Hypophosphorous acid is an acid of medium strength. Its dissociation constant is equal to $9 \cdot 10^{-2}$. Addition of a strong acid (hydrochloric and so forth) suppresses the dissociation of hypophosphorous acid. Consequently, undissociated H_3PO_2 is oxidized faster than its ions.

The unusual behavior of hypophosphorous acid as a reducing agent can be explained by the peculiarity of its structure. E. I. Orlov [4], in a study of the kinetics of the oxidation of H_3PO_2 with iodine, came to the conclusion that in a solution of hypophosphorous acid there is a tautomeric equilibrium of the two forms:

In the opinion of Orlov, the oxidation reaction with iodine proceeds by way of preliminary addition of iodine to "the unsaturated form of hypophosphorous acid $HP(OH)_2$ at the latent valencies"; as a result of the reaction the addition product of iodine to H_3PO_2 forms phosphorous acid with water which Orlov depicts in the following fashion:



Since the oxidation with iodine proceeds only in acid medium and the presence of alkali prevents the reaction, the author concluded that the acidic medium favors the transition  to  , and that this makes possible the reaction with iodine. The existence of two tautomeric forms of hypophosphorous acid has also been suggested by other investigators. Stell [5] studied the oxidation of hypophosphorous acid with iodine at low concentration of the oxidizing agent. To explain the fact that the rate of oxidation of H_3PO_2 did not depend on the concentration of oxidizing agent, he assumed that the oxidation of hypophosphorous acid into phosphorous, $H_2PO_2^- + I_2 + H_2O = HPO_3^{--} + 3H^+ + 2I^-$, proceeds by the two following reactions:

$$H_2PO_2^- + H_2O = HPO_3^{--} + 3H^+ + 2e,$$

$$2H^+ + I_2 + 2e = 2H^+ + 2I^- .$$

The rate of the first of these reactions is very low in comparison with the rate with which iodine molecules can be converted into ions, as a consequence of which, in the opinion of the author, the rate of the whole reaction does not depend on the iodine concentration.

Mitchell [6] assumed that in acidic medium the hypophosphorous acid molecules are not ionized and are found in equilibrium with a small quantity of "active" molecules of H_3PO_3,

$$H_3PO_2 + H_2O \rightleftharpoons H_3PO_3,$$

which rapidly react with iodine:

$$H_3PO_3 + I_3^- \longrightarrow H_3PO_3 + 2H^+ + 3I^-$$

Thus, the equilibrium is displaced and the rate of the reaction $H_3PO_2 + H_2O \rightleftharpoons H_3PO_3$ becomes measurable. However, Mitchell did not explain why H_3PO_3 should be an active form of hypophosphorous acid.

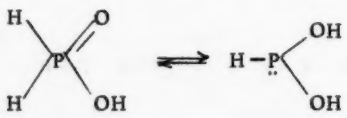
Thus, on the basis of the literature data one may conclude that in the oxidation of hypophosphorous acid, the transition of "inactive" forms into "active" has great significance and that this reaction is catalyzed by hydrogen ions.

The oxidation with iodine can, consequently, be represented by the scheme:

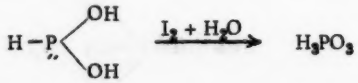
$$\underset{\text{inactive}}{H_3PO_2} \rightleftharpoons \underset{\text{active}}{H_3PO_2} \xrightarrow{I_2 + H_2O} H_3PO_3.$$

The assumption concerning the tautomerism of hypophosphorous acid was confirmed by Brodsky and his coworkers [7, 8]. L. I. Chervyatsova, D. N. Strazhesko and A. I. Brodsky [7] studied the isotopic exchange of phosphorous between H_3PO_2 containing the radioactive isotope of phosphorous and H_3PO_3 and showed that there was no isotopic exchange between them even in the presence of iodine.

The absence of isotopic exchange can serve as a new argument in favor of the existence of tautomerism of hypophosphorous acid: this fact can explain why the oxidation proceeds in two stages: a reversible (but not leading to exchange) tautomeric conversion into the active form with a coordination-unsaturated atom of phosphorous:



which is followed by the practically irreversible (and therefore not giving rise to exchange) oxidation:



A. I. Brodsky and L. V. Sulima [8], in a study of the isotopic exchange reaction of hypophosphoric acid and its sodium salt with heavy water, obtained conclusive evidence of the existence of tautomerism in hypophosphorous acid and of its absence in the anion of this acid. This work confirmed the scheme for the tautomeric conversion of H_3PO_2 set forth above.

Directing our attention to the work of Orlov [4] and the investigations of A. I. Brodsky and his coworkers [7, 8], we decided to take electropositive iodine compounds – ICl and ICl_3 as oxidizing agents for H_3PO_2, assuming that the study of these reactions would confirm the ideas of E. I. Orlov concerning the mechanism of oxidation of hypophosphorous acid by iodine solution. At the same time we aimed to develop a method for the quantitative determination of H_3PO_2 and its salts based on the use of these oxidizing agents.

EXPERIMENTAL

$NaH_2PO_2 \cdot H_2O$ and hydrochloric acid solutions of ICl and ICl_3 in which the latter was contained in the form of the complex acids $HICl_2$ and $HICl_4$ found in equilibrium with the products of their electrolytic dissociation, were taken for the experiments. These solutions were prepared from KI and KIO_3, taken in stochiometric quantities, and hydrochloric acid, calculated to obtain 0.1 N solution of ICl and ICl_3 in 0.4 N HCl solution [9, 10]. For one of the series of experiments 0.1 N solution of $NaICl_4$ was obtained from crystalline ICl_3 and an aqueous solution of sodium chloride.

Preliminary experiments showed that the reaction of hypophosphorous acid with iodine chloride proceeded with the evolution of iodine. This gave a basis for assuming that the process of oxidation can be expressed by the following equations:

$$H_3PO_2 + 4ICl + 2H_2O = H_3PO_4 + 2I_2 + 4HCl, \quad (1)$$

$$NaH_2PO_2 + 4ICl + 2H_2O = NaCl + H_3PO_4 + 2I_2 + 3HCl. \quad (2)$$

In order to confirm this hypothesis, we dissolved a batch of sodium hypophosphite in 2-3 ml of 8% HCl, shook it with excess 0.1 N hydrochloric acid solution of iodine chloride, and after several hours extracted the iodine that separated with chloroform; the chloroform extract was titrated with 0.1 N sodium thiosulfate solution. 3.99 and 4.02 g-atoms of iodine were evolved per 1 mole of $NaH_2PO_2 \cdot H_2O$.

These experiments showed that hypophosphorous acid and its sodium salt are quantitatively oxidized by iodine chloride, in agreement with equation (1) or (2). The g-equivalents of H_3PO_2 and $NaH_2PO_2 \cdot H_2O$ were equal to 0.25 g-molecular weight.

For a more detailed study of this reaction, it was necessary to establish the minimum time necessary for complete oxidation of the hypophosphorous acid into phosphoric acid with iodine chloride and also the influence of the hydrogen ion concentration on the oxidation process. According to the literature data [4], acid catalyzes the oxidation reaction of hypophosphorous acid with iodine.

For elucidating these questions, the following experiments were set up: to 5 ml of approximately 0.1 N $NaH_2PO_2 \cdot H_2O$ solution was added 25 ml of 0.1 N ICl solution and then after various intervals of time, the iodine which separated was extracted. The same experiment was set up with addition of various quantities of hydrochloric acid to the reaction mixture. The results of these experiments are set forth in Table 1.

As is evident from the data of Table 1, addition of hydrochloric acid slows the oxidation reaction of sodium hypophosphite solutions (or of solutions of hypophosphorous acid).

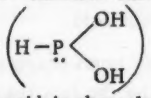
Under the conditions of the experiments, no less than 4 hours were necessary for the quantitative oxidation of sodium hypophosphite; more time was required for the oxidation of acidified NaH_2PO_2 solutions. The retarding influence of hydrochloric acid on the rate of the oxidation of hypophosphorous acid by iodine chloride can be explained by the fact that the influence of two factors is superimposed here: on the one hand, hydrochloric acid catalyzes the conversion of the "inactive form" of hypophosphorous acid into the "active", unsaturated as regards coordination bonds, form  , which speeds the oxidation; on the other hand, with increasing concentration of hydrochloric acid in the solution, the concentration of the I^+ ion is diminished, since the hydrochloric acid shifts the equilibrium $ICl_2^- \rightleftharpoons I^+ + 2Cl^-$ in the direction of formation of the complex acid $H[ICl_2]$.

TABLE 1

The influence of duration of the reaction and concentration of hydrochloric acid on the rate of oxidation of $NaH_2PO_2 \cdot H_2O$

Duration of the reaction (in hours)	Amount oxidized in the conversion, on the starting $NaH_2PO_2 \cdot H_2O$ (%)		
	Without addition of HCl	5 ml of 1 N HCl solution added	10 ml of 1 N HCl solution added
0.5	51.24	—	35.10
1	79.47	54.75	53.90
3	97.90	89.48	77.20
4	99.80	92.48	85.29
5	—	98.97	89.48
6	—	—	95.43

Since the oxidation of hypophosphorous acid with iodine chloride evidently proceeds via addition to the free electron pair of the phosphorous in $H-\ddot{P}(OH)_2$ of electropositive iodine, which acts as an electron acceptor, in the end the increased concentration of hydrochloric acid, associated with the diminished concentration of I^+ ions in the solution, lowers the rate of oxidation of hypophosphorous acid by iodine chloride.

The influence of the concentration of hydrochloric acid on the rate of oxidation of hypophosphorous acid by iodine chloride confirms the opinion concerning the existence of coordination-unsaturated forms of hypophosphorous acid , and also confirms the opinion expressed by Orlov, that the oxidation of hypophosphorous acid by iodine proceeds by way of preliminary addition of iodine to H_3PO_2.

Further investigations of the oxidative capacity of iodine halides in neutral medium reinforced our explanation of the influence of the concentration of acid on the rate of oxidation of hypophosphorous acid by iodine halides. Experiments were conducted with a solution of $NaICl_4$ (see above) in neutral medium, and also with the addition of various quantities of hydrochloric acid. The results of the determinations are set forth in Table 2.

TABLE 2

Influence of the acid concentration on the rate of oxidation of $NaH_2PO_2 \cdot H_2O$ by ICl_3 in NaCl. Weighed portions of $NaH_2PO_2 \cdot H_2O$ of 0.2600 g in 100 ml of water. For a single determination: 5 ml of solution and 25 ml of 0.1 N solution of $NaICl_4$. Temperature 60-70°

Experiment Number	Duration of reaction	Amount of 1 N HCl solution added (in ml)	Amount oxidized in the conversion, on the starting $NaH_2PO_2 \cdot H_2O$	
			(in g)	(in %)
1	60 minutes	—	0.2088	80.3
2	120 minutes	—	0.2104	80.9
3	42 hours	—	0.2597	99.9
4	60 minutes	1	0.2258	86.9
5	60 minutes	5	0.2597	99.9
6	60 minutes	20	0.2480	95.3

The data of Table 2 show that the oxidation of hypophosphorous acid by a solution of $NaICl_4$ without the addition of hydrochloric acid proceeds considerably more slowly than in a reaction mixture to which hydrochloric acid was added. The addition of small quantities of hydrochloric acid speeded the oxidation process, while great quantities of HCl led to reduction of the rate of oxidation of hypophosphorous acid.

So great a difference in the rate of oxidation of NaH_2PO_2 [$\sim$42 hours (experiment 3) and $\sim$60 minutes (experiment 5)] under the above described conditions can be explained by the fact that in both cases the hypophosphorous acid being formed (but not its salt) is subjected to the action of hydrochloric acid, added (experiment 5) or appearing (experiment 3) as a result of the reduction of ICl_3 or ICl_4^- (equation 3).

This fact can further serve as one confirmation of the fact that only the active coordination-unsaturated tautomeric form of hypophosphorous acid undergoes oxidation; this form is absent, as was shown by A. I. Brodsky and L. V. Sulima [8], in the anion of its sodium salt.

We assumed that the oxidation process of hypophosphorous acid by iodine chloride could be speeded by heating and also by dilution with water (the latter lowers the concentration of the hydrochloric acid contained in the titrated solution of iodine chloride and, therefore, increases the quantity of I^+ ions in the solution).

However, dilution of the reaction mixture with water and increasing the temperature requires somewhat modifying the method of determination, as a consequence of the fact that the complex acid $H[ICl_2]$, contained in the hydrochloric acid solution of iodine chloride, dissociates according to the equation:

$$HICl_2 \rightleftarrows H^+ + ICl_2^-$$

$$ICl_2 \rightleftarrows ICl + Cl^- .$$

Dilution with water, and also heating of the hydrochloric acid solutions of iodine chloride shifts the equilibrium to the right, in the direction of formation of a small quantity of free ICl molecules which undergo further hydrolysis with evolution of free iodine:

$$5ICl + 3H_2O \rightleftarrows 2I_2 + HIO_3 + 5HCl.$$

Thus, in such solutions it was impossible to conduct determination of hypophosphorous acid by the quantity of iodine evolved, since the chloroform also extracts the iodine formed as a result of the hydrolysis of iodine chloride. In such cases the determination has to end with decomposition of excess iodine chloride by potassium iodide with subsequent titration of the iodine with $Na_2S_2O_3$ solution.

To choose the optimal conditions for quantitative oxidation of sodium hypophosphite by ICl solution, experiments were set up in which the influence of excess iodine chloride, the time of reaction and the concentration of acid and dilution with water were studied. The results of these experiments are set forth in Table 3. For all experiments an approximately 0.1 N solution of $NaH_2PO_2 \cdot H_2O$ (0.2900 g/ 100 ml) was prepared. 5 ml of this solution was taken for each determination.

TABLE 3

The influence of various conditions on the oxidation of $NaH_2PO_2 \cdot H_2O$ by a hydrochloric acid solution of ICl

Amount added of 0.1 N ICl solution (in ml)	Amount of 0.1 N ICl solution taken up (in ml)	Quantity of water (in ml)	Temperature of the reaction mixture (in °C)	Duration of reaction (in minutes)	Amount of 1 N HCl solution added (in ml)	Amount oxidized in the conversion, on the starting $NaH_2PO_2 \cdot H_2O$	
						(in g)	(in %)
Influence of excess ICl							
10	4.90	100	40-50	60	—	0.2597	89.50
15	5.43	100	40-50	60	—	0.2878	99.23
20	5.48	100	40-50	60	—	0.2904	100.15
25	5.53	100	40-50	60	—	0.2931	101.03
Influence of the duration of the reaction							
25	2.10	100	40-50	5	—	0.1113	38.38
25	4.14	100	40-50	10	—	0.2194	75.65
25	5.31	100	40-50	30	—	0.2814	97.03
25	5.37	100	40-50	40	—	0.2846	98.10
Influence of the acid concentration							
25	5.53	100	40-50	60	1	0.2931	101.03
25	5.36	100	40-50	60	5	0.2840	97.93
25	5.06	100	40-50	60	10	0.2680	92.41
Influence of dilution with water and of the temperature of the reaction mixture							
25	3.90	—	20	60	—	0.2067	71.20
25	4.90	100	20	60	—	0.2597	89.50
25	5.50	50	40-50	60	—	0.2915	100.54
25	5.53	200	40-50	60	—	0.2931	101.03

As is evident from the data of Table 3, the oxidation of NaH_2PO_2 deteriorates without dilution with water. To obtain quantitative results it is necessary to add water heated to 40-50°; for complete oxidation, no less than 60 minutes are required; no less than a threefold excess of iodine chloride is necessary.

On the basis of these data we worked out the following method for quantitative determination: 0.25-0.3 g of hypophosphorous acid or of its sodium salt are dissolved in water in a 100 ml measuring flask. To 5 ml of the solution 100 ml of water heated to 40-50° is added and subsequently 15-20 ml of an 0.1 N solution of ICl and the solution is left for 1 hour. 10 ml of a 10% solution of potassium iodide is then added and the iodine which separates is titrated with 0.1 N sodium thiosulfate solution.

TABLE 4

Quantitative determination of $NaH_2PO_2 \cdot H_2O$ with a hydrochloric acid solution of ICl (5 ml of the starting solution taken)

Amount of the weighed portion of $NaH_2PO_2 \cdot H_2O$ (in g per 100 ml of the solution)	Amount of 0.1 N ICl solution taken up (in ml)	Amount oxidized in the conversion, on the starting $NaH_2PO_2 \cdot H_2O$	
		(in g)	(in %)
0.3170	6.00	0.3180	100.31
0.2810	5.30	0.2809	99.96

The results of the determinations are set forth in Table 4.

We also studied the reaction of sodium hypophosphite with a hydrochloric acid solution of iodine trichloride. As the experiment showed, iodine trichloride oxidizes hypophosphorous acid quanitatively into phosphoric acid. The reaction proceeds according to the equation:

$$3H_3PO_2 + 4ICl_3 + 6H_2O = 3H_3PO_4 + + 2I_2 + 12HCl \quad (3)$$

or

$$3H_3PO_2 + 4ICl_4^- + 6H_2O = 3H_3PO_4 + 2I_2 + 12HCl + 4Cl^-. \quad (3a)$$

However, we did not succeed in determining the quantity of iodine evolved, since the iodine reacts with excess iodine trichloride and is converted into iodine chloride according to the equation: $ICl_3 + I_2 = 3ICl$. Therefore, we had to determine the quantity of sodium hypophosphite (or H_3PO_2) oxidized by the amount of iodine trichloride consumed in the oxidation.

To choose the conditions for the quantitative oxidation of sodium hypophosphite or of H_3PO_2 with iodine trichloride solution, exactly the same experiments were set up for the study of the influences of the series of factors on the oxidation process as in the study of the action of iodine chloride.

The experiments showed that a reaction time of 60 minutes and a tenfold dilution with water heated to 60-70° was necessary for this. No less than a four- or fivefold excess of iodine trichloride was necessary.

TABLE 5

Quantitative determination of $NaH_2PO_2 \cdot H_2O$ with a hydrochloric acid solution of ICl_3 (5 ml of solution taken)

Amount of the weighed portion of $NaH_2PO_2 \cdot H_2O$ (in g per 100 ml of the solution)	Amount of 0.1 N ICl_3 solution used up (in ml)	Amount oxidized in the conversion, on the starting $NaH_2PO_2 \cdot H_2O$	
		(in g)	(in %)
0.2590	4.90	0.2597	100.27
0.2850	5.35	0.2835	99.49

The Method of Determination: 50-100 ml of water heated to 60-70° and 20-25 ml of 0.1 N iodine trichloride were added to 5 ml of approximately 0.1 N sodium hypophosphite solution and the solution was left for one hour. 10 ml of 10% potassium iodide solution was further added and the iodine evolved was titrated with 0.1 N sodium thiosulfate solution. It is evident from equation (3) that during the oxidation of 3 molecules of hypophosphorous acid, 4 molecules of iodine trichloride amounting to 16 equivalents of oxidizing agent, are used up. In the reaction 4 atoms of iodine are evolved, which, during the determination of excess iodine trichloride, are also titrated with sodium thiosulfate. Thus, in the oxidation of 1 molecule of hypophosphorous acid, $(16 - 4) : 3 = 4$ equivalents of oxidizing agent are actually used up.

The results of the determinations are set forth in Table 5.

SUMMARY

1. The reciprocal reactions of NaH_2PO_2 and H_3PO_2 with hydrochloric acid solutions of ICl and ICl_3 and with an aqueous solution of $NaICl_4$ reactions were studied.

2. The results of the investigations confirm the existence of two tautomeric forms of hypophosphorous acid, an inactive, coordination-saturated, and an active coordination-unsaturated, form with a free electron pair on the phosphorus.

The opinion of Orlov that the oxidation reaction of hypophosphorous acid with iodine proceeds by way of the addition to it of iodine was confirmed.

3. A method was worked out for the quantitative oxidation of NaH_2PO_2 and H_3PO_2 to phosphoric acid by iodine chloride and trichloride.

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CATALYSTS OF THE DECOMPOSITION OF HYDROGEN PEROXIDE

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Heterogeneous catalytic processes proceeding in solutions vary among themselves in a number of particulars which are not involved in gaseous contact reactions, and these processes have been studied much less than the latter. Meanwhile, these processes are very widely used, and their investigation can elucidate new aspects of the mechanism of heterogeneous catalysis, of the laws governing the choice of catalyst and of the kinetics of catalytic reactions in solutions.

Influenced by these considerations, we undertook the investigation of the catalytic action of a number of solid oxides and salts on the decomposition of aqueous solutions of hydrogen peroxide.

Hydrogen peroxide is one of the most important active compounds which appear in oxidizing reactions in solutions. Its decomposition can serve as a model reaction for more complex oxidation-reduction processes and, in addition, has great significance for biochemistry.

In our chemical literature a very considerable number of works has been devoted to the study of the catalytic decomposition of hydrogen peroxide. Arbuzov in 1914 [1] noted that the catalytic decomposition of hydrogen peroxide consisted of a reaction "the study of which, even a hundred years ago, was almost one of the most important sources for our understanding of the laws which are followed in catalytic processes."

In the investigations of Bakh [2] the decisive role of peroxides as active intermediate products in various oxidizing reactions in chemistry and biology was shown. Bakh [3] noted the probable existence of higher peroxides of hydrogen such as H_2O_4 and others.

In the middle of the 19th century, Khodnev [4] formulated the hypothesis that the decomposition of hydrogen peroxide in the presence of catalysts proceeds by way of the formation of intermediate compounds. Mendeleev [5] considered that during the decomposition of hydrogen peroxide on silver, water and silver oxide are formed; the latter during reaction with hydrogen peroxide evolves oxygen, being itself reduced to silver; this cycle is repeated many times. Silver oxide appears in the given case as an intermediate product formed during the reaction of catalyst with catalyzed substance.

The theory of intermediate compounds received further development in the works of Shpitalsky and his co-workers [6, 7] with reference to homogeneous catalysis of the decomposition of hydrogen peroxide. The works of Petin and his co-workers [8] and also the works of Bogdanov [9-11] are worth mentioning. Kobozev, Nikolaev and their co-workers [12-16] paid considerable attention to the decomposition process of hydrogen peroxide; particularly notable are their data concerning the catalytic decomposition of hydrogen peroxide under the influence of elementary ions, adsorbed on carriers, and of ammoniates of various metals.

Teletov [17] carried out detailed catalytic decompositions of hydrogen peroxide on platinum.

Pisarzhevsky and his co-workers [18-21] investigated the decomposition of hydrogen peroxide in the presence of metallic and oxide catalysts and came to the conclusion that the passage of electrons from the catalyst to the reacting molecules of hydrogen peroxide plays an essential role in the mechanism of this process and that in a number of cases it is not the solid substance itself, but its ions in solution that are responsible for the catalysis.

A chain mechanism for the decomposition of solutions of hydrogen peroxide in the presence of ions of the heavy metals was established by Haber and Wilstätter and Weiss [22-24], who gave a detailed step-by-step reaction scheme. In the recently published investigations of Emanuel and Kruglikova [25] the authors came to the conclusion that homogeneous decomposition of hydrogen peroxide ought to be considered a chain reaction with side reactions. In the opinion of certain investigators, including Kazarnovsky and Neiding [26], in the decomposition of hydrogen peroxide there takes place a chain radical reaction; in the presence of alkali this leads to the increase in the reaction rate due to the strengthening of the electrolytic dissociation of the peroxide molecule.

In contrast to homogeneous decomposition for which the basic particulars of the mechanism have been established, although details remain unclear, the mechanism of the heterogeneous decomposition of hydrogen peroxide has been less studied and the enormous experimental material which has accumulated concerning this reaction has been

insufficiently interpreted from a theoretical point of view. In this state of affairs, it is of considerable interest to trace the dependence of the catalytic activity of catalysts of the decomposition of hydrogen peroxide on the position of the elements entering into the composition of the catalysts in the Mendeleev periodic system, and on the electron and acid-base properties of the catalysts.

To conduct such a group of investigations involved methodological difficulties typical of catalysis in solution, involving such a chemically active reagent as hydrogen peroxide. Complications were produced by the appreciable solubility in hydrogen peroxide solution of a number of the catalysts investigated by us, the possibility of chemical reaction of hydrogen peroxide with the catalysts introduced by us and difusion difficulties.

Investigation of the rate of decomposition was conducted gasometrically.

The reaction apparatus was made of molybednum glass having the form of a "duck", placed in a hollow metallic cover, joined to a liquid thermostat and kept to a fixed temperature with a precision of $\pm$ 1°. The apparatus was joined to a gas burette with a fine rubber tube and was supported together with the cover on a stage of a shaking apparatus which permitted the intensity of agitation of the reaction mixture to be varied from 50 to 500 rocking oscillations per minute. As Elovich and Zhabrova [27] had shown earlier in an investigation of the catalytic hydrogenation of oil, such shaking is considerably more effective than the usual agitation for finely divided contact in liquid medium.

The order of conducting the experiments was as follows. Into the reaction apparatus, preliminarily heated to the given temperature, 20 ml of hydrogen peroxide solution was poured. After constant temperature was reached (usually after 20-30 minutes) a determined weighed portion of the catalyst equal to 0.1 g was placed in the solution. The apparatus was then closed with a stopper, the shaking apparatus was turned on and the time of beginning the reaction was noted to the second.

Comparison of the various contact reactions was conducted at 45°. It was established by preliminary experiments that both the rate of decomposition of hydrogen peroxide on the walls of the reaction vessel and the rate of homogeneous decomposition were much less than the rate of catalytic decomposition.

In working up the experiments a correction was introduced for the rate of the process of decomposition of hydrogen peroxide under analogous conditions but in the absence of catalyst. The reaction apparatus was prepared from the same sort of glass in all cases. The solution of hydrogen peroxide used in our investigations was prepared by dilution with twice distilled water of a 30% solution of perhydrol containing according to label 0.0005% chlorine, $SO_4^{=}$ 0.006%, $PO_4^{\equiv}$ 0.005%, free acid (H_2SO_4) 0.003% and insoluble residue 0.04%.

It is noteworthy that many authors, in particular Shpitalsky and Konovalova [28], Dain and Epshtein [29], demonstrated that the catalytic decomposition of hydrogen peroxide proceeds at varying rates for preparations of various origins, due to the different quantities of catalytic agents (powder, positive homogeneous catalysts, contact poisons, and so forth) they contain. Taking these observations into account, we conducted all investigations with hydrogen peroxide of the same brand and lot. The concentration of the aqueous solution of hydrogen peroxide was verified by titration with 0.1 N potassium permanganate solution.

Before arranging the systematic comparison of the activities of the catalysts under study, it was necessary to satisfy ourselves that under the chosen conditions the process would not become kinetic. For this the influence of the intensity of the shaking on the rate of decomposition of hydrogen peroxide was investigated. As is evident from Fig. 1, the rate of the reaction on magnesium oxide does not depend on the intensity of the agitation. Analogous results were obtained for other catalysts, which indicates the absence of diffusion complications.

Special experiments were set up to observe the solutions of catalysts in aqueous solution of hydrogen peroxide and to elucidate the role of homogeneous catalysis. The catalysts in the quantities employed during the measurement of the reaction rate (0.1 g) were steeped in 20 ml of 2% hydrogen peroxide solution at a temperature of 45° for 5 hours, which exceeded the duration of the majority of the kinetic experiments. Further, the solution was filtered off from the catalyst, and 5 ml of the filtrate was added to 15 ml of a 2% solution of peroxide and measurements of the rate of the decomposition of hydrogen peroxide were conducted.* The results of these experiments are set forth in Figure 2. As is evident from the figure, the filtrates of the majority of the oxides possess a noticeable catalytic action, however their catalytic activity is significantly less than the activity of solid catalysts. The filtrate of a

* In addition to this, for the inactive catalysts the filtrate practically consisted of a solution of undecomposed hydrogen peroxide and for the active — of water. Thus, in the latter case we had to do with a somewhat more dilute solution of hydrogen peroxide during the course of the experiment, which, however, could not substantially affect the catalytic activity of the solutions under investigation.

solution of hydrogen peroxide steeped with chromic oxide had considerable catalytic activity.

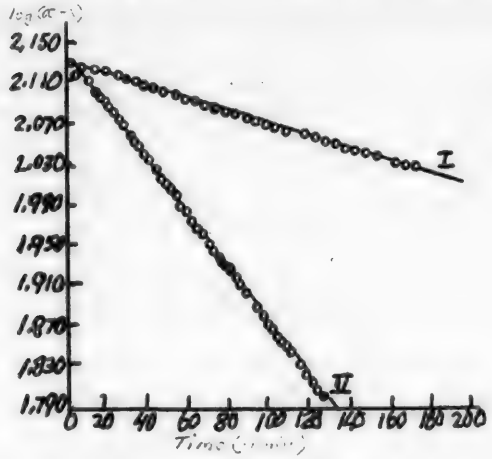

Figure 1. Non-dependence of the rate of decomposition reaction of hydrogen peroxide on the intensity of agitation of the reaction mixture (the intensity was changed in the course of the experiment from 120 to 440 rocking oscillations per minute). I—MgO; II—MgO, with antimony oxide as a promoter. a—initial quantity of H_2O_2; x—Quantity of reacted H_2O_2.

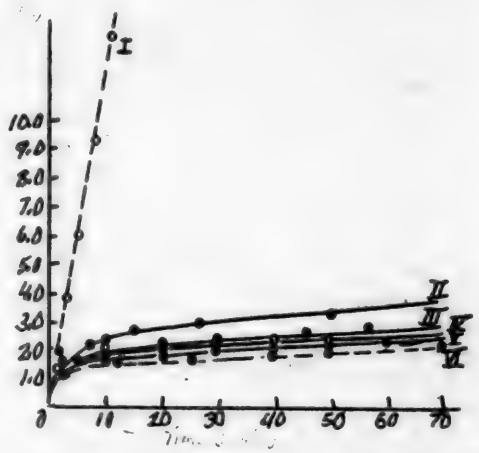

Figure 2. Decomposition of hydrogen peroxide in the presence of filtrates obtained after treatment of various oxides with a solution of hydrogen peroxide. I—Cr_2O_3 II—Fe_2O_3 III—BaO; IV—NiO; V—MgO; VI—thermal decomposition.

A second method of calculating the possible influence of homogeneous catalysis was the comparison of the actions of markedly different quantities of catalyst. The rate of heterogeneous process proceeding in the kinetic region, is directly proportional to the quantity of catalyst taken. It is difficult to expect strict adherence to this relationship during the simultaneous appreciable homogeneous catalysis of the dissolved portion of the catalyst.

Thus, from the data concerning the influence of quantity of the catalyst on the rate of the process one can obtain additional (kinetic) indications concerning the possible role of homogeneous catalysis in the decomposition of hydrogen peroxide. Such verification was conducted with a number of catalysts. The quantity of catalyst taken for the investigation was varied tenfold while keeping all other conditions constant (concentration of hydrogen peroxide, its temperature and the rate of agitation). In Fig. 3 are set forth examples of the influence of the quantity of catalyst during strong homogeneous catalysis (Cr_2O_3). In Fig. 4, the basic process is also heterogeneous (MgO). As is evident from Fig. 3, the rate of decomposition of hydrogen peroxide in the presence of chromic oxide increases considerably more slowly than the increase in quantity of catalyst and the decomposition proceeds, self-accelerated. This indicates the complexity of the process, since here, evidently, simultaneous solution of the catalyst (which was noted by the appearance of coloration) takes place, and chemical change of the form of the catalyst occurs.

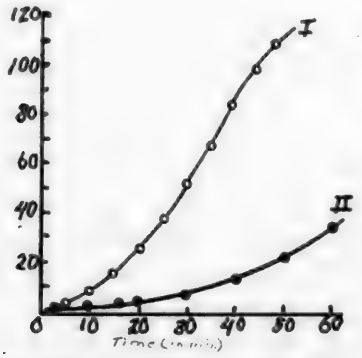

Fig. 3. Decomposition of hydrogen peroxide in presence of various quantities of chromic oxide at 45°. I—0.1 g Cr_2O_3; II—0.01 g Cr_2O_3

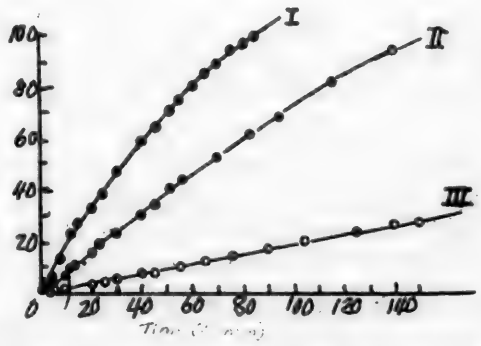

Fig. 4. Decomposition of hydrogen peroxide on magnesium oxide (quantity of magnesium oxide varied by factors of 5 and 10). I—1.0 g MgO; II—0.5 g MgO; III—0.1 g MgO.

As is evident from Fig. 4, the character of the kinetic curves for the catalysis on magnesium oxide is not changed with increase in the quantity of catalyst, but the time required to reach a given per cent of conversion falls reciprically to the increase in the quantity of catalyst.

A control for the solubility of the catalyst in the solution of hydrogen peroxide and study of the influence of the quantity of catalyst on the rate of the reaction served to elucidate the comparatively rare case when the catalytic action of added solid catalyst was dependent to a significant extent on homogeneous catalysis (dissolved contact). Thus, vanadium pentoxide taken in small quantities completely dissolved and acted purely homogeneously. Chromic oxide under these conditions was a homogeneous-heterogeneous catalyst with significant predominance of homogeneous catalysis. For iron oxide there was a small homogeneous component. The same was true of chromites.

All the remaining catalysts studied by us—manganese dioxide, nickel monoxide, copper oxide, oxides of the elements of the second group and a number of others—can be considered as typical heterogeneous catalysts of the decomposition of hydrogen peroxide in aqueous solutions. In some cases this depended on their exceedingly small solubility, in others, on the insignificant specific activity of a dissolved substance.

All the solid substances investigated by us can be divided into four groups according to their chemical and electronic properties.

In the first group go the difficultly soluble colorless salts which do not contain transition elements—lead sulfate, barium sulfate, barium carbonate, calcium carbonate, aluminum silicate.

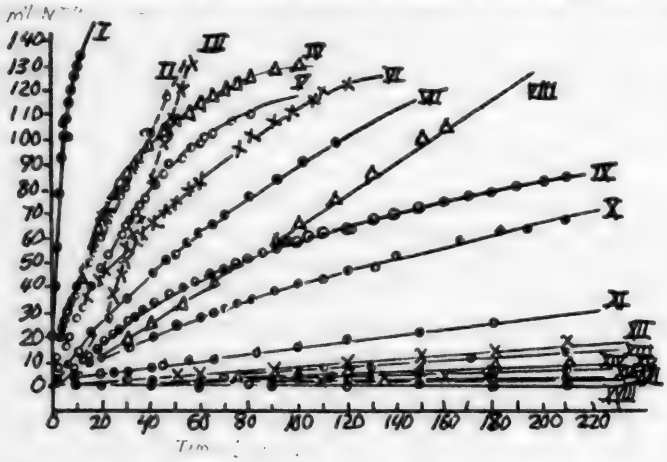

Fig. 5. Decomposition of hydrogen peroxide on various catalysts. I—MnO_2; II—V_2O_5; III—Cr_2O_3; IV—CuO; V—Fe_2O_3; VI—NiO; VII—CaO; VIII—BaO_2, IX—BaO; X—Y_2O_3; XI—MgO; XII—La_2O_3; XIII—ZnO; XIV—CdO; XV—TiO_2; XVI—aluminum silicate; XVII—Al_2O_3; XVIII—SnO_2.

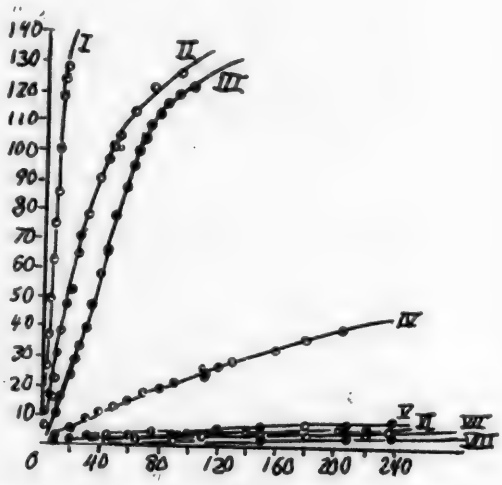

Fig. 6. Decomposition of hydrogen peroxide on the carbonates of transition and non-transition elements. I—$NiCO_3$; II—$Fe_2(CO_3)_3$; III—$MnCO_3$; IV—$MgCO_3$; V—$CdCO_3$; VI—$BaCO_3$; VII—$ZnCO_3$; VIII—$CaCO_3$.

The second group of compounds investigated contained a number of acidic and amphoteric colorless oxides—stannic oxide, silica gel, zinc oxide, aluminum oxide and the colorless oxides of the transition elements—lanthanum oxide and yttrium oxide with weakly alkaline properties.

The third group consists of colorless alkaline oxides—barium oxide, calcium oxide and magnesium oxide. All these possess an appreciable solubility which falls for aqueous solutions from barium oxide to magnesium oxide.

Into the fourth group go the typically ionic semiconductors—chromic trioxide, manganese dioxide, nickel monoxide, ferric oxide, copper oxide and others, characterized by the presence of color in the visible portion of the spectrum and appreciable conductivity at low temperatures.

Platinum black was taken as an active metallic catalyst for comparison.

The decomposition of hydrogen peroxide on various oxides and salts is presented in Figs. 5 and 6.

The data characterizing the comparative activity of various kinds of oxides and salts are presented in the table.

TABLE

Comparative activity of various oxides and salts at 45°

No.	Designation of the catalyst	Color	$K = \frac{1}{\tau_{50\%}}$ (min.$^{-1}$)	$S \frac{M^2}{g}$	$K_{sp.}$
1	$PbSO_4$		Reaction practically does not proceed. Rate of decomposition extraordinarily slow, i.e., $\frac{1}{\tau_{50\%}} < 0.001$	—	—
2	$BaSO_4$			—	—
3	$CdSO_4$			—	—
4	$ZnCO_3$	White		—	—
5	$CaCO_3$			—	—
6	$BaCO_3$			—	—
7	$MgCO_3$		0.00280	—	—
8	$MnCO_3$	Rose	0.02218	—	—
9	$Fe_2(CO_3)_3$	Light brown	0.0415	—	—
10	$NiCO_3$	Green	0.125	—	—
11	Silica gel	White	Rate of decomposition of hydrogen peroxide extraordinarily small, i.e., $\frac{1}{\tau_{50\%}} < 0.001$	300	—
12	Aluminum silicate	Cream		165	—
13	Al_2O_3			—	—
14	SnO_2	White		—	—
15	TiO_2			14.8	—
16	CdO	Brown	The same	6.0	—
17	La_2O_3*		0.0010	—	—
18	ZnO*		0.0010	20.0	0.000050
19	MgO*		0.0017	32.0	0.000053
20	Y_2O_3	White	0.0047	—	—
21	BaO		0.0076	17.5	0.00044
22	BaO_2		0.0097	—	—
23	CaO		0.0150	18.0	0.00083
24	NiO	Greyish black	0.0232	11.6	0.0093
25	Fe_2O_3	Brown	0.0294	10.2	0.002
26	Cr_2O_3**		0.0286	—	—
27	CuO	Black	0.031	—	—
28	MnO_2		0.5	6.7	0.075
29	V_2O_5***	Brown	0.045	15.0	0.003
30	$MgCr_2O_4$	Green	0.0150	49	0.0004
31	$CuCr_2O_4$	Black	0.0164	1.5	0.011
32	$CuAl_2O_4$	Light brown	0.0133	6.7	0.002
33	$FeCr_2O_4$	Red-brownish	0.00125	1.6	0.00078
34	Pt (black)	Black	Reaction completed in 1 minute		

The conventional index of activity in the decomposition of hydrogen peroxide is expressed as the reciprocal magnitude of the half time of decomposition $K = \frac{1}{\tau_{50\%}}$ (min.$^{-1}$).

Parallelly with the measurement of the catalytic activity, for a number of catalysts the magnitudes of their specific surface as measured by adsorbtion of the vapors of n-heptane were determined. These quantities are set forth in column 5 of the table.

As is evident from the table and Fig. 5, the catalyst-oxides containing transition elements and possessing an intense color, are more active than the colorless catalysts and those catalysts consisting of non-transition elements.

The difference in activity of these catalysts is very great. Thus, manganese dioxide, distinguished by its dark color and including a transition element (manganese), has a specific activity 1400 times greater than the colorless

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* In these cases the quantities $\frac{1}{\tau_{50\%}}$ were obtained by extrapolating the kinetic curves.

** The solution had a reddish color.

*** The catalyst was practically completely dissolved at the time of the experiment

oxide of magnesium, which does not contain a transition element and 171 times greater than barium oxide. Platinum black is distinguished by an exceptionally great activity. The rules applying to the oxides are accurate for the carbonates of the transition and non-transition elements.

As is evident from Fig. 6, the carbonates of nickel, iron and manganese possess the greatest catalytic activity; these contain transition elements and have an intense coloration; the colorless carbonates of magnesium, cadmium, barium and zinc oxide characterized by a significantly less activity.

Of the 14 colored catalysts investigated by us, 13 comply with the given relationship, and only one – iron chromite (Fig. 7) – is distinguished by a small activity. It is probably not by chance that the colored cadmium oxide, not containing a transition element, is little active. In comparing the activity of the catalysts investigated, it should be noted that the general rule for selection of catalysts, ensuing from the classification of the catalysts and of the catalytic processes assumed by one of us [30, 31] for reactions of the oxidation-reduction type, is demonstrably correct for the decomposition of hydrogen peroxide. The catalytic activity of the catalysts for this reaction depends on the position in the Mendeleev periodic system of the elements entering into the composition of the catalysts, and on the intensity of the coloration.

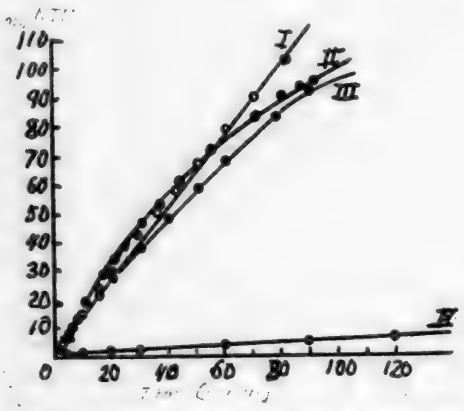

Fig. 7. Decomposition of hydrogen peroxide on chromites and aluminates. I – $CuCr_2O_4$; II – $MgCr_2O_4$; III – $CaAl_2O_4$; IV – $FeCr_2O_4$.

It should be noted that in contrast to the previously investigated process of deep oxidation of hydrocarbons [32], where the above indicated laws completely determined the activity of the contacts, in the given case a second law for the selection of catalyst is manifested that was not previously observed for the oxidation-reduction reactions; as is evident from the data set forth in the investigation of colorless oxides of the alkaline earths and rare elements, their catalytic activity increases with increase of their alkaline properties. Thus, of the oxides of the alkaline earth elements, magnesium oxide is less active than the oxides of calcium and barium. The oxides of the rare earth elements such as lanthanum, are more weakly alkaline and have less catalytic activity. Yttrium oxide is an exception. At the same time, compounds possessing acidic and amphoteric properties are distinguished by an exceedingly small catlytic activity: stannic oxide, aluminum oxide, titanium dioxide, zinc oxide, aluminum silicate. It should be noted that in all cases the method of preparing the catalysts influences the catalytic activity. In our investigations, therefore, in which in part ready made preparations were employed and in part preparations prepared by various methods, there was naturally a small deviation from the regular distribution of oxides and salts according to their catalytic activity deduced from their position in the periodic system of elements. Thus, our preparation of barium oxide was somewhat less active than calcium oxide, yttrium oxide was more active than magnesium oxide and so forth.

On the basis of our data one can speak only of general qualitative regularities.

The question concerning the detailed mechanism of the action of contact reactions involving the decomposition of hydrogen peroxide will be analyzed separately. We note here that the connection of catalytic activity with the electronic properties of the elements entering into the composition of the catalysts indicates a role for the direct exchange of electrons in the given process, while the influence of alkalinity may be associated with the increase in content of HO_2^- and O_2^- ions, which are decomposed more readily than the H_2O_2 molecule.

SUMMARY

1. The catalytic activity of a number of oxides and salts with reference to the decomposition of hydrogen peroxide in aqueous solutions was investigated.

2. In certain cases (V_2O_5, Cr_2O_3, and also partially Fe_2O_3) the homogeneous catalytic action of dissolved catalyst has an essential significance in the decomposition of hydrogen peroxide. This action is probable as a weaker secondary effect in several other cases (chromites, ferrites, oxides of the alkaline earth metals).

3. The activity of the catalysts depends on the position of the elements of which they are composed in the Mendeleev periodic system and on the chemical properties of the solid compounds. Catalysts containing transition

elements and possessing an intensive coloration as a rule are considerably more active than colorless catalysts not containing transition elements and than colored compounds not containing transition elements.

4. The catalytic activity of colorless alkaline oxides is significantly higher than the activity of colorless acid oxides and in general increases with increasing alkalinity.

5. A hypothesis concerning the various mechanisms by which the free electrons of the solids and the alkalinity of their surfaces influence the decomposition of hydrogen peroxide was proposed.

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REACTION OF DIFFICULTLY SOLUBLE SALTS WITH CATIONIC SUBSTANCES

A. G. Koblyansky

The properties of ion exchange resins and their practical uses are the subjects of thorough study at the present time [1]. However, certain peculiarities in the behavior of these substances are still insufficiently elucidated. In particular, the question of the behavior of precipitates of various difficultly-soluble salts in the presence of ion exchange resins appears not to have been studied. The present work has as its goal to at least partially fill this gap.

If in a two phase system consisting of a difficultly-soluble salt, for example $BaSO_4$ and its saturated solution, one introduces a cationic substance in, say, its sodium form RNa, then as a result of ion exchange the cationic salt will be bound by the ion exchange resin and sodium ions will pass over into the solution.

$$BaSO_4\,(\text{solid}) \rightleftarrows Ba^{2+} + SO_4^{2-}, \qquad (1)$$

$$2RNa + Ba^{2+} \rightleftarrows R_2Ba + 2Na^{+}. \qquad (2)$$

The equilibrium described by equation (1), is upset and a new portion of barium sulfate will pass over into solution. The salt will continue to dissolve as long as equilibrium in our system is not established between an aqueous solution and both solid phases—the salt and the cationic substance. In conformity with this in the moment of equilibrium there should be observed two conditions:

1) The number of barium ions absorbed by the cationic substance from the solution in unit time should be equal to the number of barium ions dislodged from the cationic substance in the same interval of time;

2) The equilibrium concentrations of barium ions and sulfate ions should satisfy the solubility product of barium sulfate.

Thus, the solubility of difficultly-soluble precipitates of a salt during their reaction with cationic substances should be determined, on the one hand by the solubility product of the salt, and on the other hand by the exchange capacity of the cationic substance, which in its turn depends on the properties of the ion exchange resin and on the properties of the adsorbed ion—on its capacity for exchange.

The behavior of the oxalates, sulfates and carbonates of the alkaline earth metals in the presence of cationic substances was studied in the present work. The bulk of the experiments were conducted with the cationic substance SBS in its sodium and hydrogen forms. Certain important conclusions were verified for sulfocarbon and P-vofatite.

The method of conducting the determinations was as follows. A weighed portion of the salt, a weighed portion of the cationic substance and a determined volume of water were introduced into a flask with a ground glass stopper. After the flask had been shaken for three hours at room temperature (20-22°), the contents of the flask were filtered through a dry filter. During the reaction of the cationic substance with the difficultly soluble salts either the corresponding free acids or their sodium salts were added dropwise o the solution:

$$SrC_2O_4 + 2RH \rightleftarrows H_2C_2O_4 + R_2Sr,$$

$$CaCO_3 + 2RNa \rightleftarrows Na_2CO_3 + R_2Ca.$$

The solution of sodium carbonate was titrated with 0.05 N hydrochloric acid in the presence of methyl red. The content of sodium oxalate was determined by titration with 0.025 N potassium permanganate. The sodium sulfate was converted into sulfuric acid, the solution was passed through a column containing H-cationite (the hydrogen form of the cationic substance) and titrated with 0.04 N sodium hydroxide in the presence of methyl red. To determine the content of free acid formed in the systems with the hydrogen form of the cationic substance, sodium hydroxide was also employed.

The data obtained during the analysis of the aqueous solution permitted the equilibrium concentration of the ions in the system under investigation to be calculated. The results of the titration directly give the equilibrium concentration of the anions in aqueous solution. Only the oxalic acid solutions in which the concentration of oxalate ions can be considered constant [2], numerically equal to the second dissocation constant ($K_2 = 6.4 \cdot 10^{-5}$), are an exception.

Knowing the equilibrium concentration of the anions and the solubility product of the difficultly-soluble salt [3], one can find the equilibrium concentration of the cations of this salt in aqueous solution. The values of the solubility products were reduced, where this was possible, to 20°.

The total quantity of salt or acid contained in aqueous solution was equivalent to the total quantity of the cations of the difficultly soluble salt adsorbed by the cationic substance. Using this relationship, one can readily calculate the equilibrium concentration of the cations of the difficultly soluble salt in the cationic substance or, in other words, the magnitude of the absorbtion by the cationite in saturated solution of the difficultly-soluble salt under static conditions:

$$\text{Magnitude of absorption} = \frac{\text{normality of the solution} \cdot \text{volume of the solution (in milliliters}}{\text{amount of the weighed portion of cationite (in grams)}} \quad \frac{\text{mg-equiv.}}{\text{g}}$$

The figures set forth in Tables 1 and 2 indicate that all the salts investigated exchange ions with the cationite and as a result partially go over into solution. This capacity of difficultly-soluble salts for ionic exchange can be given a quantitative value, showing either the equilibrium concentration of the cations of the salt under investigation in the cationite (the graph following Tables 1 and 2), or the equilibrium concentration of salt or acid in the aqueous solution. Each of these figures will uniquely characterize the solubility of the difficultly soluble salt in the presence of the given cationite only during some constant relationship of the quantities of the aqueous solution and the ion exchange resin. In our experiments the volume of water was always equal to 20 ml and the weighed portion of air-dry cationite SBS was equal to 0.4 g.

TABLE 1

Equilibrium in the system: difficultly soluble salt-water-sodium form of the cationite SBS
Amount of weighed portions of salt – 0.1 g, volume of water – 20 ml, amount of weighed portions of cationite – 0.4 g

Salt	Solubility product of salt	Equilibrium concentration		
		of anions in aqueous solution (g-ion/liter)	of cations of the salt in aqueous solution (g-ion/liter)	of cations of the salt in the cationite (mg-equiv/g)
Barium oxalate	$1.62 \cdot 10^{-7}$	$1.1 \cdot 10^{-2}$	$1.5 \cdot 10^{-5}$	1.1
Strontium oxalate	$5.6 \cdot 10^{-8}$	$9.1 \cdot 10^{-3}$	$6.2 \cdot 10^{-6}$	0.91
Calcium oxalate	$2.0 \cdot 10^{-9}$	$1.5 \cdot 10^{-3}$	$1.3 \cdot 10^{-6}$	0.15
Strontium sulfate	$2.8 \cdot 10^{-7}$	$1.1 \cdot 10^{-2}$	$2.5 \cdot 10^{-5}$	1.1
Barium sulfate	$9.3 \cdot 10^{-11}$	$4.8 \cdot 10^{-4}$	$1.9 \cdot 10^{-7}$	0.048
Barium carbonate	$7.4 \cdot 10^{-9}$	$5.1 \cdot 10^{-3}$	$1.4 \cdot 10^{-6}$	0.51
Strontium carbonate	$9.42 \cdot 10^{-10}$	$4.2 \cdot 10^{-3}$	$2.2 \cdot 10^{-7}$	0.42
Calcium carbonate	$7.4 \cdot 10^{-9}$	$5.0 \cdot 10^{-3}$	$1.5 \cdot 10^{-6}$	0.50

TABLE 2

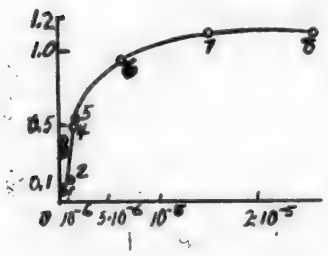
Equilibrium in the system: difficultly soluble salt-water-hydrogen form of cationite SBS
Volume of water – 20 ml, amount of weighed portion of cationite – 0.4 g

Salt	Amount of weighed portion of salt (g)	Equilibrium concentration			
		of acid in aqueous solution (g-equiv/liter)	of anions in aqueous solution (g-ion/liter)	of cations of the salt in aqueous solution (g-ion/liter)	of cations of the salt in the cationite (mg-equiv/g)
Barium oxalate	0.200	$3.1 \cdot 10^{-2}$	$6.4 \cdot 10^{-5}$	$2.5 \cdot 10^{-3}$	1.6
Strontium oxalate	0.200	$3.0 \cdot 10^{-2}$	$6.4 \cdot 10^{-5}$	$8.7 \cdot 10^{-4}$	1.5
Calcium oxalate	0.100	$2.0 \cdot 10^{-2}$	$6.4 \cdot 10^{-5}$	$3.1 \cdot 10^{-5}$	1.0
Strontium sulfate	0.100	$1.9 \cdot 10^{-2}$	$9.5 \cdot 10^{-3}$	$2.9 \cdot 10^{-5}$	0.95
Barium sulfate	0.100	$1.9 \cdot 10^{-4}$	$9.5 \cdot 10^{-5}$	$9.8 \cdot 10^{-7}$	0.0095

According to the literature data [4], the ions of the alkaline earth metals have very close exchange properties. Especially arranged experiments showed that the statistical exchange capacity [5] of the hydrogen form of cationite SBS in 0.1 N solutions of the chlorides of calcium, strontium and barium, determined by the method used in the present work, remained almost constant and equal to 1.5 mg/equiv/g. It may be concluded from this that in saturated solutions of difficultly-soluble salts the magnitude of absorption of the cationite depends little on the individual peculiarities of the ions of the various alkaline earth metals. Therefore, it can be considered that in all the systems studied, we had to do with perhaps one and the same cation and that the state of equilibrium must be determined by the concentrations of these cations. Actually, the figures set forth in Table 1 are evidence that the basic factor determining the solubility of a salt during the reaction with cationite is its solubility product. The less the solubility product of the salt, the more difficult the exchange between the ions and the cationite, and the less the magnitude of the absorption of the cationite in a saturated solution of this salt. This condition is true not only of salts of the same acid – for sulfates, oxalates, carbonates separately; it appears to be true also in relation to the entire aggregate of difficultly-soluble salts of calcium, strontium, and barium, regardless of which anion these salts contain. Salts with solubility products of the order of 10^{-7} react quite well with cationite. The equilibrium concentration of these salts for the sodium form of cationite SBS amounts to more than 1 mg-equiv/g. In salts with solubility products close to 10^{-10}, the ion exchange is insignificant.

Only strontium carbonate ($K_s = 9.4 \cdot 10^{-10}$) appears to be an exception to this rule: in the presence of the sodium form of the cationite (Table 1) this salt dissolves better than calcium oxalate ($K_s = 2 \cdot 10^{-9}$).

In systems containing the hydrogen form of cationite (Table 2), the oxalates of the alkaline earth metals display enhanced solubility in comparison with the sulfates: strontium oxalate ($K_s = 5.6 \cdot 10^{-8}$) passes over into solution more readily than strontium sulfate ($K_s = 2.8 \cdot 10^{-7}$). This phenomenon is caused by the fact that oxalic acid in comparison with sulfuric acid is a much weaker electrolyte. Therefore, in an equilibrium system: oxalate of an alkaline earth metal-water-hydrogen form of cationite, along with the two conditions for equilibrium, noted above, one additional condition must be observed: the equilibrium concentrations of the ions and the undissociated molecules of oxalic acid must satisfy its dissociation constants. The hydrogen ions displaced from the cationite as a result of ion exchange will give with the oxalate ions undissociated molecules, and thus will exert supplementary dissolving action on the oxalate residue.



Dependence of the magnitude of absorption of the sodium form of cationite SBS in saturated solutions of oxalates, sulfates and carbonates of the alkaline earth metals on the equilibrium concentrations of the cations of these metals in aqueous solution. 1) $BaSO_4$, 2) CaC_2O_4, 3) $SrCO_3$, 4) $CaCO_3$, 5) $BaCO_3$, 6) SrC_2O_4, 7) BaC_2O_4, 8) $SrCO_4$.

The functional dependence linking the equilibrium concentrations of the ions of the alkaline earth metals in aqueous solution and in the ion-exchange resin (Table 1), can be depicted graphically.

The smooth form of the curve shows that in calculating the equilibrium concentrations of the ions without taking account of their activity coefficients, we obtain comparable results which basically reflect correctly the regularities which are observed during the distribution of the cations between the aqueous solution and the ion exchange resin.

A sharp increase in the equilibrium concentrations of the cations of the alkaline earth metals in the ion exchange resin is observed only in the initial portion of the curve for exceedingly dilute solutions (10^{-6}–10^{-5} g-ion/liter). The cationite extracts approximately 1 g-equiv/g from a solution containing 10^{-5} g-ion/liter. During further increase in the concentrations of the water solution, the magnitude of the absorption for cationite SBS changes very slowly. As was noted above, the static exchange capacity of the hydrogen form of cationite SBS in 0.1 N solutions of the chlorides of calcium, strontium and barium amounts to 1.5 mg-equiv/g.

It is evident from Table 2 that the hydrogen form of cationite SBS absorbs the ions of the alkaline earth metals more poorly than its sodium form.

The data concerning the solubility of difficultly-soluble salts in

TABLE 3

Change in the acidity of an aqueous solution in the system: mixture of sulfates of barium and strontium-water-hydrogen form of cationite SBS as a function of the strontium sulfate content. Weighed portions of barium sulfate – 1 g, volume of water – 20 ml, weighed portion of cationite – 0.4 g

Amount of strontium sulfate introduced (in g)	Amount of 0.03817 N sodium hydroxide (in ml) consumed in the titration of 10 ml of the solution
0.05	4.57
0.02	2.30
0.01	1.11
–	0.20

the presence of ion exchange resins can be utilized for resolving certain practical problems. If the solubility product of a salt is very small, then a small admixture of another more soluble electrolyte should strongly affect the equilibrium concentrations of the ions in aqueous solution. Study of the behavior of mixtures of the sulfates of barium and strontium showed (Table 3) that even in the presence of 1% strontium sulfate, the acidity of the solution was sharply increased.

The use of the process of ion exchange as a rapid method for assaying the purity of difficultly soluble salts is suggested.

SUMMARY

1. It was established that in the reaction of difficultly-soluble salts with cationite in the presence of water the partial solution of these salts proceeds as a result of ion exchange.

2. The magnitude of the absorption for cationite SBS was determined in saturated solutions of the oxalates, sulfates, and carbonates of the alkaline earth metals under static conditions.

3. It was shown that the basic factor determining the solubility of difficultly-soluble salts in the reaction with cationite is the solubility product of these salts.

4. A curve was drawn for the magnitude of the absorption of cationite SBS in saturated solutions of the oxalates, sulfates and carbonates of the alkaline earth metals as a function of the equilibrium concentrations of the cations of these metals in aqueous solution.

5. A method was proposed for detecting insignificant admixtures of strontium sulfate in barium sulfate, based on the marked difference in the solubility of these salts during their reaction with cationite.

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* See Consultants Bureau Translation, page 153.

CHEMICAL REACTIONS IN VANADIUM PENTOXIDE – POTASSIUM SULFATE AND VANADIUM PENTOXIDE – POTASSIUM PYROSULFATE SYSTEMS

G. K. Boreskov, V. V. Illarionov, R. P. Ozerov and E. V. Kildisheva

Vanadium pentoxide, the basic component of vanadium catalysts for oxidizing sulfur dioxide, in the pure form possesses weak catalytic activity, which is rapidly increased by addition of salts of the alkaline metals [1]. Newmann [2] attempted to elucidate this sharply expressed promoter action by forming alkaline metavanadates.

It was, however, shown by further investigations [3] that the metavanadates of potassium and sodium are destroyed under the conditions of the catalytic oxidation of sulfur dioxide with the formation of the corresponding sulfates and pyrosulfates. It was also discovered that in the working vanadium catalysts, the bulk of the alkaline addition was found in the form of the sulfate or the pyrosulfate, regardless of what kind of compound was initially introduced into the catalyst.

At a comparatively low temperature and high partial pressure of sulfuric anhydride, that is, under conditions corresponding to the final stage of the oxidation of sulfur dioxide, pyrosulfate is formed; at higher temperatures and low concentrations of SO_3 in the gas, the sulfate of the alkaline metal is stable.

On the basis of what has been related we sought with interest, from the point of view of elucidating the mechanism of the promoter action of compounds of potassium on vanadium pentoxide, to study the systems $V_2O_5-K_2SO_4$ and $V_2O_5-K_2S_2O_7$, which are only unconditionally models to the extent that in vanadium catalysts, along with V_2O_5, they are present in the early stages of oxidation of vanadium, in quantities which depend on the temperature and the content of SO_2 in the gas.

EXPERIMENTAL

The system $V_2O_5-K_2SO_4$ was investigated, in a preliminary fashion, by one of us and M. A. Guminskaya. The data obtained, of a qualitative character, showed the presence of a eutectic with a melting point of about 450°.

Vanadium pentoxide, and potassium sulfate and pyrosulfate were the starting materials in our investigations. Commercial vanadium pentoxide was converted into ammonium vanadate by treatment with ammonia solution. The precipitate was dissolved in hot water and freed from mechanical admixtures. We proceeded further by the method of one of us and E. E. Ruderman [4]. The preparation obtained by this method was heated in a stream of oxygen at 400-450° for one hour. The latter operation was added by us in order to exclude the possible partial reduction of the pentoxide in the process of mechanical grinding [5]. Chemically pure potassium sulfate was twice recrystallized.

Potassium pyrosulfate was prepared according to the method of Cambi and Bozza [6] by heating potassium sulfate at 420-450° in a stream of dry air containing 5% SO_3. The gaseous mixture was obtained by preliminary conversion of the mixture of dry air with 5% SO_2 on a vanadium catalyst at 470°. The melting point of the potassium pyrosulfate was comparatively low, as a result of which the preparation was covered with a layer of melted pyrosulfate and the process of further sulfatization was retarded. Therefore, the salt treated by us was cooled in a stream of dry SO_3 to 350°, and then was finely divided in a stream of dry air and again treated with the indicated gaseous mixture at high temperature. This sequence of treatment was repeated until complete conversion of the sulfate into the pyrosulfate was achieved. The criterion of purity was the melting point. The preparation obtained agreed according to analysis, exactly with the composition $K_2S_2O_7$ with m.p. 407°, in contrast to that indicated by the Italian authors at 414.2° [6].

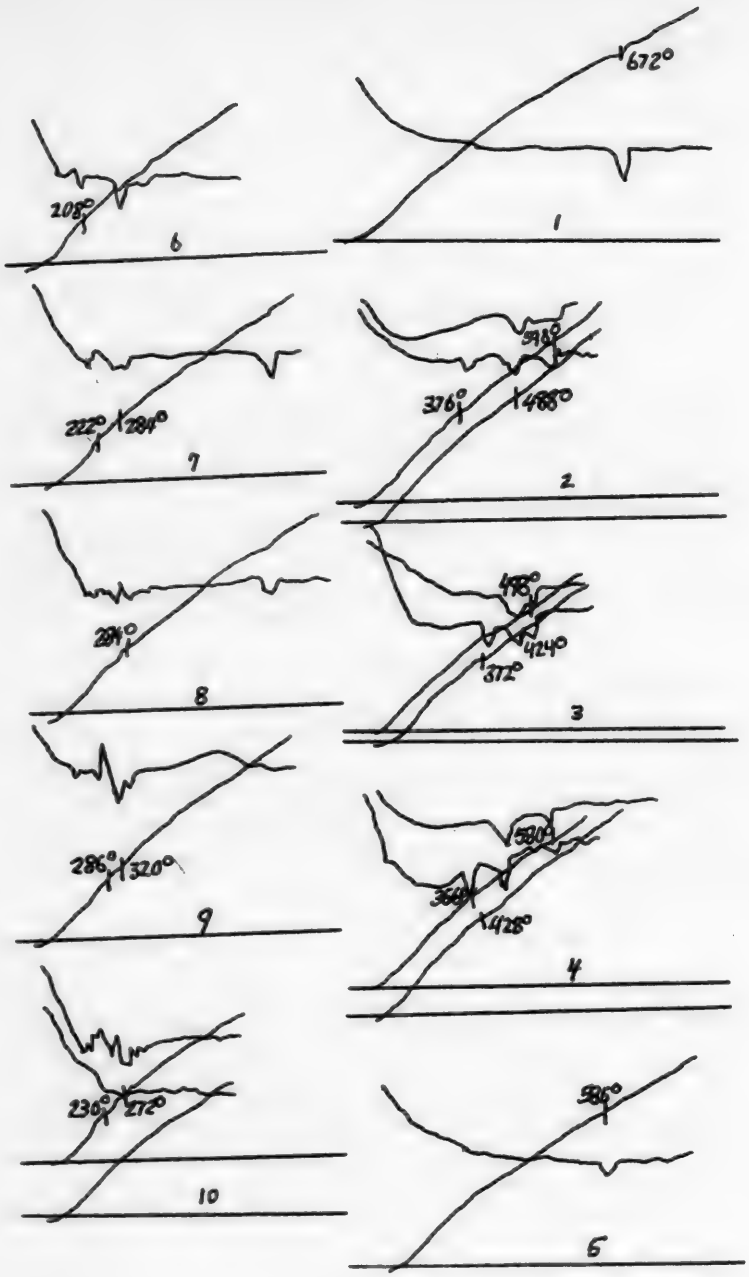

Fig. 1. Thermograms of fusion cakes of the systems $V_2O_5-K_2SO_4$ and $V_2O_5-K_2S_2O_7$. 1) Pure V_2O_5; 2) Batch of 0.2 mole-portion of K_2SO_4; 3) Batch of 0.5 mole-portion of K_2SO_4; 4) Batch of 0.8 mole-portion of K_2SO_4; 5) Pure K_2SO_4; 6) Pure $K_2S_2O_7$; 7) 0.2 mole-portion of $K_2S_2O_7$; 8) 0.3 mole-portion of $K_2S_2O_7$; 9) 0.5 mole-portion of $K_2S_2O_7$; 10) 0.7 mole-portion of $K_2S_2O_7$. In all thermograms, with the exception of the third, the upper transcription – the starting mixture, the lower transcription – repeated heating; in the third, the reverse is true.

All the initial compounds obtained were investigated roentgenographically. Roentgenological analysis showed that vanadium pentoxide possessed a rhombohedral lattice with parameters a = 11.48 Å, b = 4.36 Å, and c = = 3.55 Å, which was in agreement with the data published earlier [7, 8]. The roentgenograms obtained with powdered potassium sulfate and pyrosulfate were identical with the literature data [9].

Method of Investigation

Carefully ground preparations were mixed in the necessary proportions. The mixtures, in quantities of about 5 g, were stirred in a quartz Stepanov vessel (capacity 6-8 ml), in which the thermal investigations were conducted. The system $V_2O_5-K_2SO_4$ was investigated in open vessels but the system $V_2O_5-K_2S_2O_7$ in sealed vessels. Batches of the second system were placed in vessels which were then evacuated with a Gede pump to 10-15 mm residual pressure and sealed under a vacuum in order to avoid substantial change of the composition during heating, as a result of thermal decomposition and the volatilization of SO_3 associated with it (due to the high dissociation tension of pyrosulfate). The recordings of the cooling curves were conducted on a potentiometric installation with a chromal-alumel thermocouples. Compensation was accomplished on a sensitive slide wire cylinder and the current strength in the auxiliary circuit was held constant all the time with the aid of a manganin resistance box and controlled with a galvanometer. The rate of cooling was of the order of 2° per minute.

The heating curves were taken on a Kurnakov pyrometer with platinum-platino-rhodium thermocouples.

The fusion cakes obtained were ground in an agate mortar

and subjected to roentgenostructural and chemical analyses.

The roentgenograms of all samples were taken with a copper emission spectrum in a truncated Debye chamber with a cell diameter of 92 mm. Inasmuch as the copper emission stimulates the secondary isotropic emission of vanadium, fogging the roentgenograms, with the exception of samples with a low V_2O_5 content, aluminum foil was placed around the film.

The content of SO_3, V_2O_5, and V_2O_4 was determined by chemical analysis of the fusion cake.

The System $V_2O_5-K_2SO_4$. The heating curves and the cooling curves were taken for the pure components and their mixtures in one tenth molar portions (Fig. 1).

The greatest interest attaches to the endothermic effect on the heating curve, observed in the entire composition interval and lying close to 380°. On the cooling curve this effect is absent, nor arising during repeated heating of the mixtures, which is evident from comparison of the thermograms on Fig. 1. If we take into account, aside from this, that this effect is not detected in the pure components taken separately, and is most strongly expressed in a mixture of $0.5V_2O_5-0.5K_2SO_4$, then it must be explained by reaction of vanadium pentoxide with potassium sulfate.

The remaining thermal effects observed, compared on the curves of cooling and heating and repeated heating, can be comparatively briefly discussed.

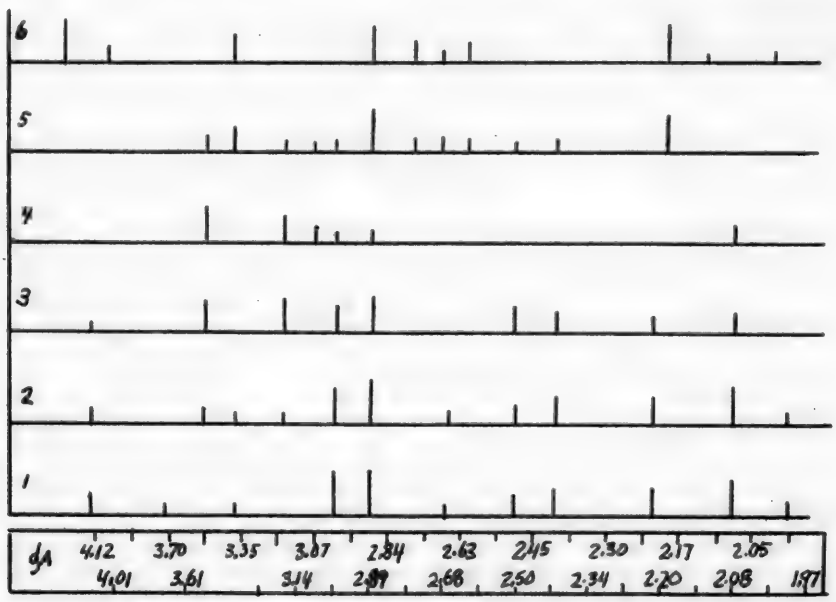

Fig. 2. Roentgenogram chart of the system $V_2O_5-K_2SO_4$. 1) Pure K_2SO_4, 2) 40% V_2O_5, 3) 50% V_2O_5, 4) 60% V_2O_5, 5) 70% V_2O_5, 6) pure V_2O_5.

It is very material that both connodes of the eutectic breaks in continuity lie on different temperature levels. This appears to be an unmistakable demonstration of the formation of compounds, although a dystectic maximum was not established by us.

All the fusion cakes were ground and subjected to roentgenologic structural investigation. While the roentgenograms of the pure components were legible, the fusion cakes gave a very strong fogging, evoked by the presence of an isotropic vitreous phase, and a number of somewhat weakened diffraction lines. The maximum intensity of these lines on the roentgenogram of a fusion cake containing 0.5 mole-portions of V_2O_5 could not be related to one of the starting components and belonged, consequently, to an unknown compound among them. On Fig. 2 is set forth a part of the scheme of roentgenograms.

TABLE 1

Composition of the fusion cake		Amount of weighed sample (in g)	Theoretical content of V_2O_5	Aqueous extract		Residue		Total content calculated as V_2O_5	Content of SO_3	
V_2O_5 (in moles)	K_2SO_4 (in moles)			V_2O_5	V_2O_4	V_2O_5	V_2O_4		Theoretical	In the aqueous extract
0.7	0.3	0.4995	0.3496	0.0091	None	0.3342	0.0033	0.3469	0.0688	0.0650
0.6	0.4	0.4999	0.3051	0.0036	0.0050	0.2857	0.0107	0.3065	0.0895	0.0856
0.5	0.5	0.5007	0.2534	0.0058	None	0.2374	0.0074	0.2513	0.1113	0.1100
0.3	0.7	0.5004	0.1501	0.0102	•	0.1365	0.0019	0.1488	0.1610	0.1608

• Not determined.

The results of the thermal and roentgenostructural analysis uniquely indicates the formation of compounds between V_2O_5 and K_2SO_4.

The composition of this compound, evidently, does not correspond to a simple 1 to 1 relationship, but lies very close to it in the direction of being more rich in V_2O_5. This thesis is confirmed by the high-temperature thermal effects in fusion cakes with 0.5 and 0.6 mole-portions of V_2O_5. In the first it is found at 490°, and in the second at 520°. Roentgenographically this was confirmed by the fact that on the powder roentgenogram of a fusion cake with 0.5 mole-portion of V_2O_5, there is present a weakly-expressed maximally-intense K_2SO_4 line. It is possible, however, that the compound being formed corresponds in composition to $V_2O_5 \cdot K_2SO_4$, but the observed phenomena are evoked by the absence of complete internal equilibrium.

The endothermically formed compound is not stable and is readily decomposed. During the leaching of the fusion cakes, ground to a powder, with water, their sulfate portion is entirely extracted with water along with a very small quantity of vanadium oxide, of which the water-insoluble residue is entirely composed . Both in the water extract and in the insoluble residue along with V_2O_5 there was also detected a lower form of vanadium oxide — V_2O_4, absent in the pure starting preparation, which indicates the partial formation of potassium vanadico-vanadate. The formation of these compounds ($V_2O_4 \cdot 5V_2O_5 \cdot K_2O$, $V_2O_4 \cdot 4V_2O_5 \cdot K_2O$ and others) was observed by Prandtl and Murschhauser [10] and Canneri [11] during the crystallization of fusion cakes of vanadium pentoxide with alkalis at a ratio $V_2O_5 : K_2O > 1$. It is not without interest to note that the color of the fusion cakes formed is considerably darker than that of solidified fused V_2O_5. The darkest color was in the fusion cake with 0.5 mole-portion of V_2O_5. The fusion cakes ground to powder had an intense brownish-olive color, markedly different from the color of ground vanadium pentoxide. The results of the chemical analyses are set forth in Table 1. It should be noted that both the boiling and the subsequent treatment of the insoluble portion with sodium hydroxide were conducted in a stream of nitrogen bubbled through liquid placed in a flask with a ground top. The total results of the thermal and roentgenostructural investigations permit us to construct a diagram of the composition of the system $V_2O_5 - K_2SO_4$ (Fig. 4).

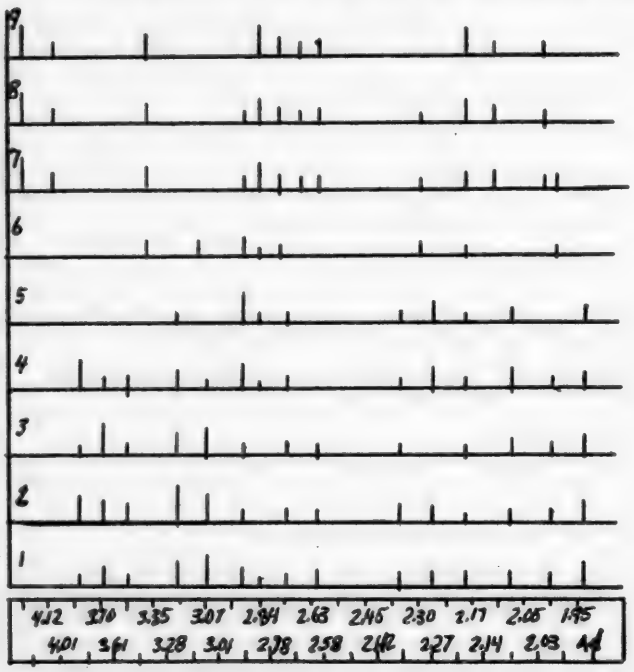

Fig. 3. Roentgenogram chart of the system $V_2O_5 - K_2S_2O_7$.
1) Pure $K_2S_2O_7$; 2) 10% V_2O_5; 3) 20% V_2O_5; 4) 30% V_2O_5; 5) 40% V_2O_5; 6) 50% V_2O_5; 7) 60% V_2O_5; 8) 70% V_2O_5; 9) pure V_2O_5.

• Not determined.

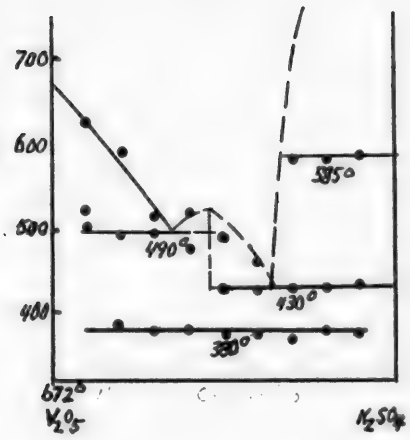

Fig. 4. Fusion curve of the system $V_2O_5-K_2SO_4$.

The system $V_2O_5-K_2S_2O_7$. Thermal investigations of the system $V_2O_5-K_2S_2O_7$ according to the cooling curves did not permit the presence of heat effects to be established in the region of mixtures containing less than 0.5 mole-portions of V_2O_5. This depended on its capacity to form glass readily.

A larger number of effects was detected on the heating curves. At a temperature close to 222° an endothermic effect is observed which depends on the polymorphic conversion of potassium pyrosulfate. At a temperature of the order of 272° an exothermic effect is observed which reaches a maximum at the ratio $V_2O_5: K_2S_2O_7 = 1:1$. On the cooling curve and on the repeated heating curve it is absent over all the interval of composition. Evidently, the maximum is linked with the formation of a compound of possible composition $V_2O_5 \cdot K_2S_2O_7$.

In connection with the fact that equilibrium is not completely established, unreacted pyrosulfate is present in the form of a separate phase and evokes an endothermic effect. The latter is increased in proportion to the increase of $K_2S_2O_7$ content, which is linked with the second polymorphic conversion of this component at 350°. The curves corresponding to compositions containing more than 0.4 mole-portion of V_2O_5, show the presence of one more endothermic effect, the position of which is displaced from 668° in pure V_2O_5 to 556° in mixtures containing 0.6 mole-portions of this component. These are the only effects displayed on the cooling curves. They may be interpreted as associated with the liquidus lines.

TABLE 2

Composition of the fusion cake		Amount of weighed sample (in g)	Theoretical content of V_2O_5	Aqueous extract		Residue		Total content calculated as V_2O_5	Content of SO_3	
V_2O_5 (in moles)	$K_2S_2O_7$ (in moles)			V_2O_5	V_2O_4	V_2O_5	V_2O_4		Theoretical	In the aqueous extract
0.7	0.3	0.4995	0.3123	0.0107	None	0.2914	0.0021	0.3044	0.1178	0.1155
0.3	0.7	0.4999	0.1172	0.0139	0.0042	0.0981	0.0017	0.1185	0.2408	0.2387

The increased tendency of melts containing potassium pyrosulfate to vitrify extraordinarily complicates the roentgenographic investigation. All the roentgenograms of the mixtures are strongly fogged which does not permit definite conclusions to be made regarding the origin of certain lines of the roentgenogram. A significant change in the comparative intensity of the diffraction lines on the roentgenograms of the fusion cakes rich in potassium pyrosulfate, is to be explained, evidently, by the partial hydration under the action of the water vapor of the air during the preparation of the samples for exposure, which leads to the formation of $KHSO_4$ (Fig. 3).

It is necessary to note that the compound formed during the leaching with water is also unstable, similarly to what was observed in the sulfate system (Table 2).

SUMMARY

1. Thermographic and roentgenographic investigations of the systems $V_2O_5-K_2SO_4$ and $V_2O_5-K_2S_2O_7$ were conducted.

2. In the system $V_2O_5-K_2SO_4$, the formation of a compound was detected, close in composition to $V_2O_5 \cdot K_2SO_4$, with a melting point around 500°. The eutectic point between this compound and potassium sulfate lies below 430° and corresponds to an approximate content of V_2O_5 of 0.4 mole-portion. An approximate composition diagram was constructed for this system.

3. In the system $V_2O_5-K_2S_2O_7$, melts with a great content of pyrosulfate (above 0.4 mole-portion) possessed low melting points and readily vitrified during cooling. During heating of mixtures of V_2O_5 and $K_2S_2O_7$, an exothermic effect was detected at 275°, which can be explained by the formation of the compound $V_2O_5 \cdot K_2S_2O_7$.

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Scientific Institute
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DISTRIBUTION OF ISOMORPHIC AND ISODIMORPHIC COMPONENTS BETWEEN THE SOLID AND LIQUID PHASES DURING CRYSTALLIZATION FROM AQUEOUS SOLUTIONS

II. EQUILIBRIUM IN CERTAIN SYSTEMS WITH SCHOENITE (PICROMERITE) TYPE DOUBLE SALT COMPONENTS

G. I. Gorshtein and N. I. Silantyeva

Equilibrium in the System $CoSO_4 \cdot (NH_4)_2SO_4 - NiSO_4 \cdot (NH_4)_2SO_4 - H_2O$ at 20°

Double salts of the schoenite type ($MgSO_4K_2SO_4 \cdot 6H_2O$, where in place of Mg there may be Co^{++}, Ni^{++}, Fe^{++}, Zn^{++}, Cu^{++}, Mn^{++}, Cd^{++}, in place of $K - NH_4^+$, Rb^+, Cs^+, Tl^+, in place of S – Se, Te, Cr) are usually truly isomorphic and form a continuous series of solid solutions. Accordingly, the study of systems with these components presents considerable interest for the elucidation of the laws governing the distribution of isomorphic components between the solid and liquid phases.

In the investigation of the system $CoSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ the concentrations of cobalt in the crystals and in the mother liquors were determined by means of potentiometric titrations with potassium ferricyanide in an ammoniacal medium. The concentration of nickel was determined gravimetrically by means of precipitation with dimethylglyoxime. At low nickel concentrations, the nickel was preliminarily isolated as the solid dimethylglyoxime by the method of Peshkova [2].

The results of the experiments are given in Table 1 and in Figure 1 (the equilibrium composition diagram) and Figure 2 (the distribution diagram).

TABLE 1

Equilibrium in the System $CoSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ at 20° [I – % $CoSO_4(NH_4)_2SO_4 \cdot 6H_2O$; II – % $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$]

Experiment No.	Results of the analysis				II		Distribution coefficient	
	of the solid phase		of the mother liquor		in the solid phase	in the salt portion of the mother liquor	D equilibrium (Ni, Co)	D equilibrium (Co, Ni)
	I	II	I	II				
1			16.70	0	0	0	–	–
2	88.14	8.58	15.66	0.47	8.91	2.9	3.3	0.30
3a	84.20	13.32	15.22	0.71	13.7	4.5	3.5	0.29
3b	82.83	13.04	15.08	0.68	13.7	4.3	3.5	0.29
4a	76.04	21.08	14.05	1.19	21.8	7.8	3.3	0.30
4b	76.86	21.37	13.97	1.16	22.0	7.65	3.5	0.29
5	57.17	37.28	10.31	2.30	39.6	18.2	3.0	0.34
6a	21.80	74.20	4.82	5.19	77.4	51.9	3.2	0.31
6b	20.60	73.40	4.11	5.35	78.2	56.6	2.8	0.36
7a	13.64	80.67	3.30	5.68	85.7	63.3	3.4	0.29
7b	13.37	81.56	3.28	5.69	85.5	63.4	3.4	0.29
8a	7.82	89.85	1.97	7.16	92.0	78.5	3.2	0.31
8b	7.82	84.10	1.97	7.34	91.4	78.8	2.9	0.34
9a	6.03	88.66	1.55	7.38	93.7	82.6	3.1	0.32
9b	6.77	87.69	1.61	7.40	93.6	82.1	3.1	0.32
10			0	8.45	100.00	100.00	–	–

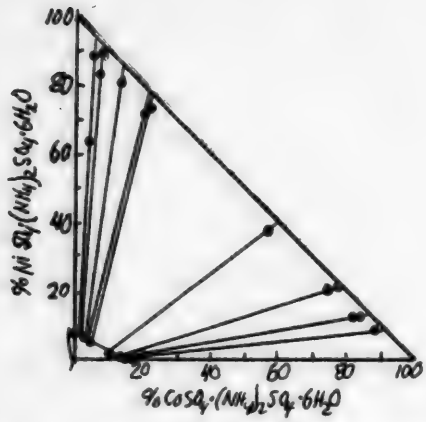

Fig. 1. Equilibrium composition diagram for the system $NiSO_4(NH_4)_2SO_4-CoSO_4(NH_4)_2SO_4-H_2O$ at 20°.

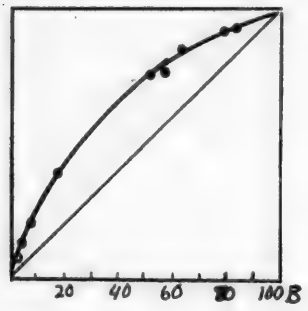

Fig. 2. Distribution diagram for the system $NiSO_4(NH_4)_2SO_4-CoSO_4(NH_4)_2SO_4-H_2O$ at 20°. A) % $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in the solid phase; B) % $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in the salt portion of the mother liquor.

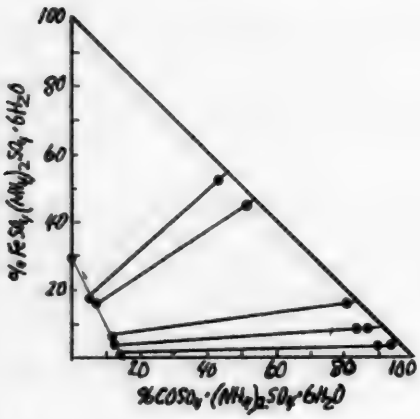

Fig. 3. Equilibrium composition diagram for the system $FeSO_4(NH_4)_2SO_4-CoSO_4(NH_4)_2SO_4-H_2O$ at 20°.

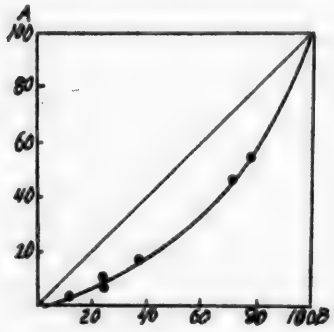

Fig. 4. Distribution diagram for the system $FeSO_4(NH_4)_2SO_4-CoSO_4(NH_4)_2SO_4-H_2O$ at 20°. A) % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in the solid phase; B) % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in the salt portion of the mother liquor

TABLE 2

Equilibrium in the system $FeSO_4(NH_4)_2SO_4-CoSO_4(NH_4)_2SO_4-H_2O$ at 20°. [I – % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$; II – % $CoSO_4(NH_4)_2SO_4 \cdot 6H_2O$]

Experiment No.	Results of the analysis of the solid phase		of the mother liquor		I		Distribution coefficient	
	I	II	I	II	in the solid phase	in the salt portion of the mother liquor	$D_{equilibrium}$ (Fe, Co)	$D_{equilibrium}$ (Co, Fe)
			0	16.70				
1a	4.04	94.02	1.89	14.08	4.09	11.83	0.318	3.14
1b	3.89	89.51	1.89	14.02	4.06	11.87	0.315	3.17
2a	9.43	86.67	4.29	13.26	9.68	23.91	0.336	2.97
2b	9.21	83.84	4.29	13.26	9.66	23.91	0.331	3.02
3a	16.08	80.92	6.94	11.90	16.44	36.83	0.330	3.03
3b	14.91	78.37	6.92	11.92	15.64	36.83	0.319	3.13
4a	44.88	50.75	16.60	6.02	46.56	73.38	0.315	3.17
4b	44.47	51.03	16.47	5.83	46.18	73.81	0.317	3.15
5a	52.13	43.98	18.37	4.99	53.92	78.63	0.318	3.14
5b	52.29	44.06	18.41	5.03	54.22	78.53	0.330	3.03
			28.75	0				

TABLE 3

Equilibrium in the System $NiSO_4(NH_4)_2SO_4-FeSO_4(NH_4)_2SO_4-H_2O$ at 20°. [I – % $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$; II – % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$]

Experiment No.	Results of the analysis						Total degree of crystallization, α	II		Distribution coefficient	
	of the solid phase		of the mother liquor		starting solution			in the solid phase	in the salt portion of the mother liquor	$D_{equilibrium}$ (Ni, Fe)	$D_{equilibrium}$ (Fe, Ni)
	I	II	I	II	I	II					
			0	28.75							
1a	10.54	83.80	0.26	26.70	1.30	32.5	0.28	88.5	99.0	13.2	0.076
1b	10.91	86.30	0.26	26.60	1.30	32.5	0.28	88.7	99.0	12.8	0.078
2a	19.90	76.79	0.54	24.79	3.0	29.6	0.27	79.2	98.0	12.1	0.083
2b	19.60	76.30	0.54	24.79	3.0	29.6	0.27	79.4	98.0	11.9	0.084
3a	30.40	66.47	0.86	22.61	4.39	28.59	0.38	69.6	96.3	12.0	0.083
3b	29.50	65.64	0.84	22.79	4.39	28.59	0.37	70.5	96.4	11.6	0.086
4a	49.50	43.92	1.68	17.50	7.19	20.79	0.38	46.1	91.2	12.1	0.083
4b	50.94	44.70	1.69	17.49	7.19	20.79	0.38	46.1	91.1	11.7	0.085
5a	60.74	34.05	2.13	14.70	14.06	1.13	0.49	35.2	86.9	11.3	0.081
5b	59.30	34.28	2.20	14.14	14.06	1.13	0.49	35.4	86.5	11.6	0.086
6a	74.17	20.68	3.66	9.76	13.96	11.47	0.55	21.5	72.7	10.0	0.10
6b	73.63	20.71	3.65	9.53	13.96	11.47	0.55	22.4	72.3	10.0	0.10
7a	76.63	18.26	3.70	8.96	12.20	10.18	0.50	18.8	70.8	10.43	0.096
7b	73.63	18.66	3.86	8.81	12.20	10.18	0.49	19.6	69.5	9.38	0.11
10a	81.08	14.30	4.42	7.37	9.11	8.11	0.36	14.66	62.5	9.85	0.10
10b	78.55	13.70	4.48	7.75	9.11	8.11	0.33	14.22	63.3	10.40	0.096
11a	81.69	12.59	4.49	6.49	10.14	7.02	0.34	13.00	59.2	10.0	0.10
11b	81.72	12.58	4.47	6.49	10.14	7.02	0.34	13.98	59.2	10.0	0.10
12a	85.77	9.69	5.68	5.33	–	–	–	10.00	48.4	8.33	0.12
12b	86.22	9.81	5.69	5.31	–	–	–	10.11	48.2	8.33	0.12
13a	85.82	6.33	6.38	3.60	22.56	4.08	0.67	6.59	36.1	7.69	0.13
13b	87.84	6.14	6.34	3.62	22.56	4.08	0.68	6.32	36.3	8.33	0.12
14a	91.93	5.32	6.32	2.87	16.7	3.11	0.59	5.40	31.2	8.33	0.12
14b	91.76	5.47	6.34	2.88	16.7	3.11	0.59	5.50	31.2	7.69	0.13
15a	93.22	3.64	7.56	2.10	12.94	2.23	0.40	3.75	21.7	7.14	0.14
15b	90.70	3.70	7.53	2.12	12.94	2.23	0.40	3.80	22.0	7.14	0.14
16a	94.70	2.02	7.45	1.04	14.06	1.13	0.48	2.05	12.3	7.14	0.14
16b	94.10	1.96	7.50	1.05	14.06	1.13	0.47	2.00	12.2	7.14	0.14
			8.45								

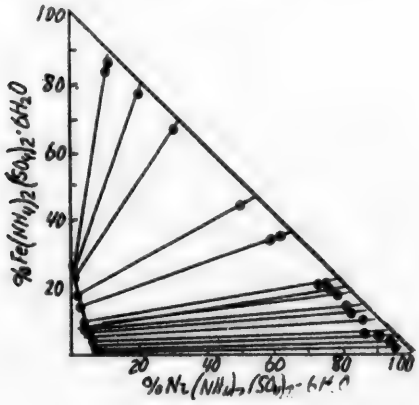

Fig. 5. Equilibrium composition diagram for the system $FeSO_4(NH_4)_2SO_4$ - $NiSO_4(NH_4)_2SO_4-H_2O$ at 20°.

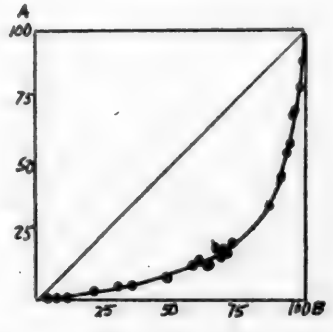

Fig. 6. Distribution diagram for the system $FeSO_4(NH_4)_2SO_4-NiSO_4(NH_4)_2SO_4-H_2O$ at 20°. A) % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in the solid phase; B) % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in the salt portion of the mother liquor.

TABLE 4

Equilibrium in the System $NiSO_4(NH_4)_2SO_4-FeSO_4(NH_4)_2SO_4-H_2O$ at 0°. [I – % $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$; II – % $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$]

Experiment No.	Results of the analysis of the solid phase		Results of the analysis of the mother liquor		Results of the analysis starting solution		Total degree of crystallization, a	II in the solid phase	II in the salt portion of the mother liquor	Distribution coefficient $D_{equilibrium}$ (Ni, Fe)	Distribution coefficient $D_{equilibrium}$ (Fe, Ni)
	I	II	I	II	I	II					
33a	15.39	71.58	0.30	18.00	1.87	28.93	0.38	82.61	98.35	12.5	0.080
33b	16.34	75.73	0.33	18.20			0.37	81.96	98.21	12.1	0.082
30a	26.07	67.53	0.57	16.53	3.53	22.44	0.52	71.40	96.66	11.5	0.086
30b	26.80	69.91	0.49	15.83			0.55	71.99	96.99	12.6	0.079
31a	32.78	57.41	0.73	13.91	2.62	17.17	0.30	62.92	95.08	11.2	0.089
31b	33.97	59.13	0.76	14.53			0.27	59.96	95.04	12.7	0.078
32a	55.20	40.21	1.19	10.90	3.87	12.46	0.29	41.80	90.16	12.7	0.078
32b	54.97	41.05	1.20	10.87			0.30	42.47	90.05	12.1	0.083
45a	82.24	11.66	2.94	4.33	7.35	4.73	0.44	12.10	59.56	10.7	0.093
45b	84.89	12.29	2.92	4.26			0.45	12.54	59.33	10.2	0.098
43a	84.29	10.11	3.31	3.34	7.97	3.79	0.46	10.56	50.22	8.5	0.12
43b	82.11	9.89	3.31	3.41			0.46	10.47	50.74	8.8	0.11
42a	87.59	7.23	3.25	2.54	8.93	2.69	0.53	7.50	43.87	9.7	0.10
42b	85.93	7.32	3.76	2.62			0.48	7.68	41.06	8.4	0.12
40a	87.20	4.44	4.36	1.65	8.16	1.77	0.42	4.71	27.45	7.7	0.13
40b	90.76	4.52	4.68	1.61			0.39	4.67	25.60	7.1	0.14

TABLE 5

Values of the equilibrium distribution coefficients according to the experimental data of Hill [3]

1	2		3		
Per cent of Ni salt in the salt portion of the mother liquor	$D_{equilibrium}$ (Ni, Zn)	Per cent of Ni salt in the salt portion of the mother liquor	$D_{equilibrium}$ (Ni, Cu)	Per cent of Zn salt in the salt portion of the mother liquor	$D_{equilibrium}$ (Zn, Cu)
14.1	3.6	3.9	12.0	14.0	2.5
14.0	3.9	3.9	12.9	13.4	2.8
20.6	3.9	5.5	16.6	25.7	2.7
28.3	3.9	5.6	16.7	25.7	2.7
27.3	4.4	10.3	15.7	46.5	4.0
43.5	5.7	10.0	16.7	46.5	4.0
42.4	5.8	22.0	17.8	68.0	9.2
74.0	2.9	21.5	20.0	68.0	12.7
		51.5	13.0		
		51.5	13.6		

As is evident from the data of the last column of Table 1, the system $CoSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ behaves ideally over the entire concentration range of both components. The magnitude of the equilibrium distribution coefficient of cobalt salt in nickel salt $D_{equilibrium\ (Co,\ Ni)}$ is equal on the average to 0.31; the magnitude of the equilibrium distribution coefficient of nickel salt in cobalt salt is equal on the average to 3.2.

Equilibrium Distribution of Components in the System $FeSO_4(NH_4)_2SO_4 - CoSO_4(NH_4)_2SO_4 - H_2O$ at 20°

The method of analysis was the same as that employed in the investigations of the system $CoSO_4 - FeSO_4 - H_2O$ [1].

The results of the experiments are set forth in Table 2 and in Figs. 3 and 4.

The system $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O - CoSO_4(NH_4)_2SO_4 \cdot 6H_2O - H_2O$ at 20° can be considered ideal over the entire concentration range of the components. The average magnitude of the equilibrium distribution coefficient of iron salt in relation to cobalt salt $D_{equilibrium\ (Fe,Co)}$ is equal to 0.32; the opposite average magnitude of the equilibrium

distribution coefficient of cobalt salt in relation to iron salt $D_{equilibrium\ (Co,Fe)}$ is equal to 3.1.

Equilibrium in the System $FeSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ at 20°.

The method of analysis employed was the same as in the investigation of the system $FeSO_4 - NiSO_4 - H_2O$ [1]. The results of the experiments are set forth in Table 3 and in Figs. 5 and 6.

This system, in contrast to the two preceding, was not ideal over the entire range of concentrations of the components.

The magnitude of the equilibrium distribution coefficient of nickel salt in the iron salt $D_{equilibrium\ (Ni, Fe)}$ varied from 7.1 to 13 and on the average was equal to 10.1; in view of this, the system can be considered ideal only within a limited concentration range at the edges of the distribution diagram.

In one of these intervals the magnitude of $D_{equilibrium\ (Ni, Fe)}$ retains a value in the range 12-13, during the change in the concentrations of nickel salt in the salt portion of the mother liquor of from 0 to 15%, and accordingly in the solid phase of from 0 to 35%. At the other edge of the diagram the magnitude of the equilibrium distribution coefficient of iron in the nickel salt $D_{equilibrium\ (Fe, Ni)}$ retains values in the limits 0.13-0.14, at concentrations of iron salts in the salt portion of the mother liquor of from 0 to 30% or, accordingly, in the solid phase of from 0 to ~5%.

Equilibrium in the System $FeSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ at 0°.

The results of the experiments are set forth in Table 4.

The equilibrium distribution of components at 0° has exactly the same character as at 20°.

DISCUSSION OF RESULTS

Hill [3] and others studied the equilibrium distribution of isomorphic components in a number of systems with salts of the schoenite (picromerite) type at a temperature of 25°. They advanced the general proposition that such systems are not ideal and that the value of $D_{equilibrium}$ for them is unilaterally changed by increase in the concentration of one of the components from 0 to 100%.

This conclusion was hardly substantiated, however, by the experimental data of these investigators.

As an illustration we present (Table 5) the values of the equilibrium distribution coefficients calculated by us from the data of Hill and co-workers for three of the systems which they studied:

1. $ZnSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$.
2. $CuSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$.
3. $CuSO_4(NH_4)_2SO_4 - ZnSO_4(NH_4)_2SO_4 - H_2O$.

The considerable and irregular dispersion of the values of $D_{equilibrium}$ in these systems in conjunction with the small number of points indicates the inadequate reliability of the data of these authors.

Our investigations, in contrast to the general hypothesis of Hill and co-workers, have established that the systems $CoSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$ and $CoSO_4(NH_4)_2SO_4 - FeSO_4(NH_4)_2SO_4 - H_2O$ with components of the schoenite (picromerite) type are ideal at 20° over the entire range of concentration of components. Deviations from the mean values of $D_{equilibrium}$ in our data on the average did not exceed ± 5% relatively, which simultaneously serves as confirmation of the reliability of the methods of investigation employed by us.

Deviations from the ideal for the system

$$NiSO_4(NH_4)_2SO_4 - FeSO_4(NH_4)_2SO_4 - H_2O$$

are evidently associated with very significant difference in the solubility of both salts, which possibly evokes in its turn a more acute difference in the magnitudes of the coefficients of activity of the components in the liquid and solid phases.

The changes in the magnitudes of $D_{equilibrium}$ have a smooth character.

Although one of the three systems investigated by us exhibits certain deviations from the ideal, the mean values of the equilibrium distribution coefficients for these systems satisfy the formula presented in [1]: $D_{equilibrium\ (A, C)} = D_{equilibrium(A, B)} \cdot D_{equilibrium(B, C)}$. Actually, $D_{equilibrium\ (Ni, Co)} = 3.3$, $D_{equilibrium\ (Co,Fe)} = 3.1$; hence $D_{equilibrium\ (Ni, Fe)}$ is determined by calculation $3.3 \cdot 3.1 = 10.2$, as contrasted with a mean value 10.0 obtained from the experimental data.

The dependence between the concentrations of the components in the equilibrium mother liquors is expressed in a tetragonal diagram for the two ideal systems as a straight line. For the third system: $NiSO_4(NH_4)_2SO_4$ – $FeSO_4(NH_4)_2SO_4$ – H_2O this relationship has a more complex character.

SUMMARY

1. The equilibrium at 20° in the systems:

$$CoSO_4(NH_4)_2SO_4 - NiSO_4(NH_4)_2SO_4 - H_2O$$
$$CoSO_4(NH_4)_2SO_4 - FeSO_4(NH_4)_2SO_4 - H_2O$$

and in the system $FeSO_4(NH_4)_2SO_4$ – $NiSO_4(NH_4)_2SO_4$ – H_2O at 20° and 0° was studied.

2. It was established that the first two systems are ideal at 20° over the entire range of concentrations of both isomorphic components. The following values for the equilibrium distribution coefficients were found: for the system: double salt of nickel – double salt of cobalt – water $D_{equilibrium(Ni,\ Co)} = 3.2$, $D_{equilibrium(Co,\ Ni)} = 0.31$; for the system: double salt of cobalt – double salt of iron – water $D_{equilibrium(Co,\ Fe)} = 3.1$, $D_{equilibrium\ (Fe,\ Co)} = 0.32$.

3. It was found that the system $NiSO_4(NH_4)_2SO_4$ – $FeSO_4(NH_4)_2SC_4$ – H_2O is not ideal at 20° over the entire concentration range, but only in fixed limits at the edges of the equilibrium diagram. The value of the equilibrium distribution coefficient for admixture of Ni during the crystallization of the double salt of iron amounts at 20° and at 0° to 12.5; the value of the equilibrium distribution coefficient for Fe^{++} admixture during the crystallization of the double salt of nickel amounts to 0.14 at 20° and at 0°.

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INVESTIGATION OF COMPLEX FORMATION BETWEEN THE BISMUTH ION AND THE IONS OF TARTARIC ACID

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The ions of tartaric and citric acids can form complex compounds with the ions of bismuth which are water soluble at all pH values.

The data in the literature concerning the composition of these complex compounds are rather contradictory [1-5]. In addition, in the majority of the indicated cases the composition of the tartaric and citric complexes was considered without taking into account the pH of the medium, although the content of tartaric acid ions and the hydrolysis of bismuth salts is determined by the pH value of the medium.

The object of the present investigation was the study of the chemistry of the complex-formation reactions of the Bi^{3+} ion with the ions of tartaric acid, taking into account the influence of the pH of the medium by a potentiometric method, in order to establish the composition of the complex ions and to calculate the instability constants of these complex ions. Chemically pure metallic bismuth was taken as the recording electrode and a saturated calomel electrode was used as the standard. The measurements were conducted on a potentiometer of the Rapp type.

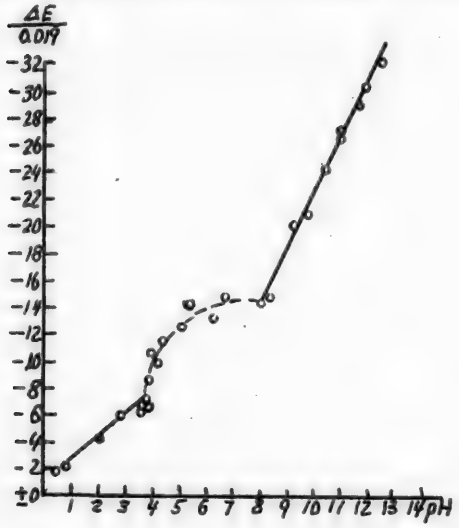

Fig. 1. The potential of a bismuth electrode as a function of the pH at $[Bi^{+3}]$ = 0.01 mole/liter and of $Na_2C_4H_4O_6$ = 0.2 mole/liter.

The investigation of the dependence of the potential of the bismuth electrode on the pH of the medium at a constant concentration of $[Bi^{+3}]$ of 0.01 mole/liter and of $Na_2C_4H_4O_6$ of 0.2 mole/liter is presented in Fig. 1.

It is evident from the data of Fig. 1 that there are 3 clearly expressed zones: the first – in the acid region at pH 1-4 is characterized by rectilinear dependence of the electrode potential on pH; in the second – at pH ≈ 4-9 a rectilinear dependence of the electrode potential on pH is not observed; the third zone – in alkaline media at pH ≈ 9-13.5 is characterized by a rectilinear dependence of the electrode potential on the pH of the medium.

Taking into account the acid-base nature of the bismuth ion, which has the capacity to undergo hydrolysis at pH 2-3, and the peculiarities of tartaric acid, in which the first ionization constant is of the order of $K_1 = 1 \cdot 10^{-3}$ and the second $K_2 = 9 \cdot 10^{-5}$, it is natural to suppose that a reciprocal reaction of the bismuth ion with the bitartrate ion proceeds in the first zone and that a reciprocal reaction of the bismuth ion with tartrate and hydroxyl ions proceeds in the third zone. The second zone appears to be an intermediate region where formation of basic bismuth salts of indeterminate composition is possible. In this zone, i.e., at pH 4-8, if the concentration of sodium tartrate is less than 0.1 mole/liter, and $[Bi^{+3}]$ = 0.01 mole/liter, the precipitation of a white amorphous precipitate is observed. The chemical analysis of this precipitate showed that it consisted of a mixture of $Bi(OH)_3$ with tartrate, i.e., of basic bismuth salt and tartaric acid.

The first and third zones were of interest for the potentiometric method and were carefully studied to elucidate the chemical composition of the compounds obtained in solution and to calculate the ionization constants of these compounds.

In the first zone, i.e., in the region of low pH values, reciprocal reaction of bismuth ions with bitartrate ions

should occur. The potential values of the bismuth electrode as a function of the concentration of the bitartrate ion are presented in Fig. 2.

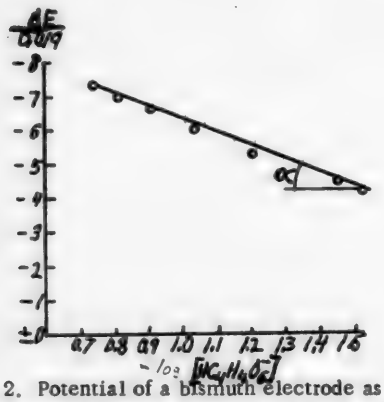

Fig. 2. Potential of a bismuth electrode as a function of the concentration of $HC_4H_4O_6^{-1}$ at pH 2.62 and $[Bi^{+3}] = 0.01$ mole/liter.

It is evident from the data of Fig. 2 that the tangent of the angle of inclination of the straight line plotted with the coordinates $\frac{\Delta E}{0.019} - \log [HC_4H_4O_6^-]$, exhibits the coordination number of the bismuth ion with reference to the bitartrate ion; in the given case equal to 4.1, i.e., close to 4. Consequently, 1 ion of bismuth coordinates 4 ions of bitartrate. The bitartrate ion was titrated with a solution of bismuth nitrate at pH 2-3 to verify these data. The appearance of stable turbidity formed as a result of the hydrolysis of bismuth nitrate (Table 1) served as indicator.

It is evident from column 5 of Table 1 that at pH 2.4-2.9 the ratio $\frac{[HC_4H_4O_6^-]}{[Bi^{+3}]} \approx 4$.

Thus, the results of visual titration are confirmed by the data of the potentiometric investigation. On the basis of these data one can assert that at pH 2-3 the bismuth ion forms a complex ion with the bitartrate ion of composition $Bi(HC_4H_4O_6)_4^{-1}$, and the instability constant of this complex ion (concentrated is expressed by the equation:

$$K_{instability_1} = \frac{[Bi^{+3}]\,[HC_4H_4O_6^{-1}]}{[Bi(HC_4H_4O_6)_4^{-1}]}.$$

TABLE 1

Amount of 0.5 mole/liter of $Na_2C_4H_4O_6$ taken	Amount of 0.1 mole/liter of $Bi(NO_3)_3$ (in ml) consumed	pH of the final solution	Amount of $HC_4H_4O_6^-$ contained in m-moles	$\frac{HC_4H_4O_6^-}{[Bi^{+3}]}$
5.00	1.20	2.40	0.515	4.3
5.0	1.80	2.65	0.784	4.3
5.0	2.10	2.68	0.821	3.9
2.0	0.91	2.77	0.372	4.0
4.0	1.83	2.77	0.744	4.0
5.0	2.60	2.82	1.000	3.8
2.0	1.06	2.88	0.427	4.0
2.0	1.05	2.88	0.427	4.0
2.0	1.06	2.90	0.435	4.1
4.0	2.6	3.92	0.675	2.6
5.0	2.0	4.72	0.436	2.2
5.0	1.4	5.29	0.135	0.96

The instability constant was calculated from the reduced ionization equation of the complex ion and the electrode potential equation by the formula:

$$\log K_{instability_1} = \frac{\Delta E}{0.019} - \log [complex] + 4 \log [HC_4H_4O_6^-].$$

The average value of $K_{instability_1} = 5 \cdot 10^{-9}$.

The detailed potentiometric investigations are presented in Table 2.

Investigation of the third (alkaline) zone at pH 8-13, showed that for each ion of bismuth one ion of tartrate was required, since the tangent of the angle of inclination of the straight line plotted with the coordinates $\frac{\Delta E}{0.019} - \log [C_4H_4O_6^{-2}]$, was equal to 1.

TABLE 2

$[Bi^{+3}]$ (in mole/liter	$Na_2C_4H_4O_6$ (in mole/liter)	pH	e.m.f. (in volts)	$\frac{\Delta e.m.f.}{0.019}$	$[HC_4H_4O_6^-]$ (in mole/liter)	$K_{instability_1}$
0.01	0	1.1	0.025	—	–	–
0.01	0.10	2.62	0.106	−4.26	0.0299	$4.36 \cdot 10^{-9}$
0.01	0.20	2.62	0.125	−5.26	0.0598	$7.08 \cdot 10^{-9}$
0.01	0.30	2.62	0.140	−6.05	0.0897	$5.7 \cdot 10^{-9}$
0.01	0.40	2.63	0.152	−6.70	0.1196	$4.1 \cdot 10^{-9}$
0.01	0.50	2.62	0.160	−7.10	0.1495	$4.0 \cdot 10^{-9}$
0.01	0.60	2.62	0.1648	−7.37	0.1794	$4.5 \cdot 10^{-9}$

Visual titration of the tartrate ion with $Bi(NO_3)_3$ solution at pH 13 showed that for 0.25 ml of 1 mole/liter $Na_2C_4H_4O_6$, 2.5 ml of 0.1 mole/liter of $Bi(NO_3)_3$ were consumed, which gives the ratio $[C_4H_4O_6^{-2}]/[Bi^{+3}] = 1$.

TABLE 3

Concentration of Bi^{+3} = 0.01 mole/liter

$K_2C_4H_4O_2$ (in mole/liter)	pH	e.m.f. (saturated calomel electrode) (in volts)	$\frac{\Delta e.m.f.}{0.019}$	$K_{instability_2}$
0	1.1	0.025	—	—
0.10	10.0	0.4043	−19.95	$1.1 \cdot 10^{-31}$
0.10	11.25	0.4810	−24.00	$0.56 \cdot 10^{-31}$
0.10	11.9	0.4970	−24.84	$7.2 \cdot 10^{-31}$
0.10	12.83	0.5410	−27.16	$2.14 \cdot 10^{-31}$
0.10	13.40	0.610	−30.80	$0.25 \cdot 10^{-31}$

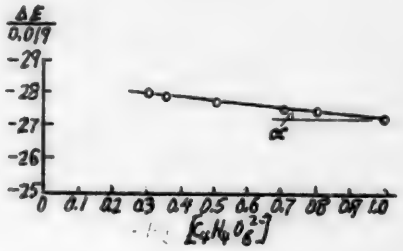

Fig. 3. Potential of a bismuth electrode as a function of the concentration of $[C_4H_4O_6^{-2}]$ at pH 13 and $[Bi^{+3}]$ = 0.01 mole/liter; tan α = 1.

Consequently, 1 ion of tartrate is required for 1 ion of bismuth in alkaline medium. In addition to the tartrate ion the OH' ion can react with the bismuth ion in alkaline medium. This follows from Table 3 and Figs. 1 and 4, in which the bismuth potential measurements are presented as a function of the pH of the solution.

It follows from the potentiometric determinations (Fig. 4) that 1 ion of bismuth coordinates 3 OH' ions in the alkaline tartrate complex.

Thus, the following composition can be assigned to this complex ion: $[Bi(OH)_3C_4H_4O_6]^{-2}$.

The results of the calculation of the instability constants according to the potentiometric investigations and the formula:

$$\log K_{instability_2} = \frac{\Delta e.m.f.}{0.019} - \log [complex] + \log[C_4H_4O_6^{-2}] + 3pH - 3pK_W$$

are presented in Table 3. The mean value of the instability constant is of the order of 10^{-31}.

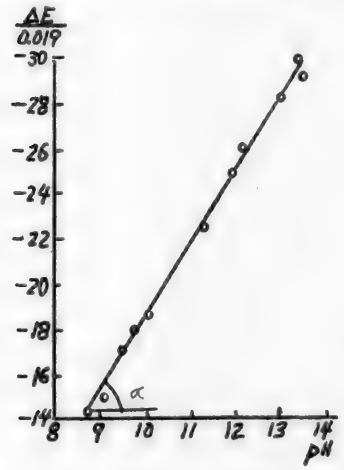

Fig. 4. Potential of a bismuth electrode as a function of pH at a concentration of $K_2C_4H_4O_6$ equal to 0.1 mole/liter, and of Bi^{+3} = 0.01 mole/liter; tan α = 3.0.

TABLE 4

$Na_2C_4H_4O_5$ (in mole/liter)	Bi (in g/50 ml)	[complex] (in mole/liter)	$K_{equilibrium}$
0.01	0.04	0.004	0.40
0.03	0.102	0.010	0.33
0.05	0.166	0.016	0.32
0.08	0.272	0.026	0.32
0.10	0.296	0.028	0.28
0.10	0.296	0.028	0.28
		Mean	0.32

Having established the composition of the alkaline tartrate complex ion of bismuth and having calculated its ionization constant from the potentiometric data, starting from the solubility product of hydrated bismuth oxide $K_S\ Bi(OH)_3 = 4.3 \cdot 10^{-31}$, we attempted to verify the value of the instability constant by the solubility method. The investigations essentially consisted in treating the solid phase $Bi(OH)_3$ in a constant assigned alkali concentration with a solution of sodium tartrate with its concentration varying according to changes in the concentration of $Na_2C_4H_4O_6$ determined in a bismuth solution (by electrolysis).

We further assumed that the following complex-formation reaction occurred:

$$Bi(OH)_3 + C_4H_4O_6^{-2} \rightleftarrows [Bi(OH)_3C_4H_4O_6]^{-2}.$$

The equilibrium constant of this reaction is expressed by the equation:

$$K_{equilibrium} = \frac{[complex]}{[C_4H_4O_6^{-2}]}.$$

The solid phase $Bi(OH)_3$ was taken as a constant quantity and always occurred in excess. $K_{equilibrium}$ was calculated from the experimental data (Table 4). Knowing the value of the latter and $K_{s\ Bi(OH)_3}$, one can determine the instability constant from the equation:

$$K_{instability_2} = \frac{K_{s\ Bi(OH)_3}}{K_{equilibrium}} = \frac{4.3 \cdot 10^{-31}}{0.32} = 13.4 \cdot 10^{-31}.$$

The numerical values of the instability constants of the alkaline tartrate complex of bismuth obtained by the two distinct methods were in excellent agreement.

SUMMARY

Depending on the pH of the medium, the bismuth ion gives two complex compounds with the ions of tartaric acid: 1) in acidic medium at pH≈ 2-3, the complex ion $Bi(HC_4H_4O_6)_4^{-1}$ with a $K_{instability} = 10^{-9}$ and 2) in alkaline medium at pH≈ 9-14 the complex ion $[Bi(OH)_3C_4H_4O_6]^{-2}$ with a $K_{instability} = 10^{-31}$.

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* See Consultants Bureau Translation, page 1977.

THE THERMODYNAMICS OF OXIDE PHASES OF VARIABLE COMPOSITION

I. THE THERMODYNAMICS OF FERROUS OXIDE

S. M. Ariya, M. P. Morozova and L. A. Shneider

It is generally known that the subgroup elements have a characteristic capacity to form oxides of variable composition. This phenomenon has practical as well as theoretical significance. However, although we already have available a detailed enough structural formula for the phase of variable composition, and in a number of cases know with sufficient precision the extent of the region of homogeneity of many elements, the laws governing the changes in the extent of the region of homogeneity of oxides during the transition from one element to another are still not clear.

It is natural that before this question will be reconciled with the positions of the periodic law and the theory of the chemical bond, similar compounds, the bertollides of N. S. Kurnakov, must be studied not only structurally but also thermodynamically. However, up to the present time, such thermodynamical investigation of oxide phases of variable composition is almost wholly lacking.

The simplest way to acquire an understanding of the thermodynamics of oxides of variable composition appears to be the study of their equilibria (at variable composition) with gaseous oxidizing-reducing systems.

The present work is one of the links in a proposed chain of investigations devoted to the thermodynamics of ferrous oxide.

As is well known, ferrous oxide is thermodynamically stable only above 572°; in the opinion of the majority of authors [1], the stoichiometric phase – FeO – is metastable at all temperatures, while the thermodynamically stable phase has the composition FeO_{1+x}, where x depends both on the temperature and on the pressure of oxygen in the gaseous phase which coexists with ferrous oxide.

The work of Darken and Garri [2] was devoted to determination of the enthalpies of formation of ferrous oxides of variable composition; they investigated the equilibrium of ferrous oxide with CO_2/CO mixtures, but at an adverse temperature range*, in which the entire region of homogeneity of ferrous oxide corresponded to a change in the ratio P_{CO_2}/P_{CO} of several hundredths at an absolute value of around 0.3 for this ratio.

In addition to this, Darken and Garri obtained data for the magnitude of the region of homogeneity which were noticeably different from the results of the investigations of other authors, which compels one to treat their data with a certain degree of caution.**

Investigation of the Equilibrium $FeO_{1+x+y} + yCO \rightleftarrows FeO_{1+x} + yCO_2$

Ferrous oxide containing, according to the spectral analysis data, the following admixture: Ni, Co ~ 0.001, Mn < 0.001, Cu ~ 0.001, V ~ 0.001, Cr, W < 0.01%, served as the object of the investigation.

The equilibrium was investigated at 1104 and 1182°K in a circulation apparatus (delivery of gas 5 liters/hour); the composition of the solid phase was established with the use of spring scales. The gaseous mixture at the attainment of equilibrium was analyzed, as usual, by absorption of carbon dioxide gas by alkali, and of carbon monoxide in an ammoniacal solution of Cu_2Cl_2. Particular attention was paid to maintaining constant temperature: with the use of a photothitration relay the temperature was kept constant with a precision of ± 0.2°. The observed dependence of the composition of the solid phase on the ratio of the partial pressure of carbon dioxide to carbon monoxide is given in Table 1 and in Fig. 1.

The isotherms show, first of all, that the content of oxygen in the solid phase is not a linear function of the partial pressure of atomic oxygen in the gaseous phase (or, which is the same thing, a linear function of the ratio P_{CO_2}/P_{CO}).

* 1100-1350°.

** For example, according to the data of Jette and Foote [3] and Pfeil [5], at 1200° the oxygen-rich ferrous oxide contains 24.3% oxygen, while, according to the data of Darken and Garri, it contains 25.3%.

TABLE 1

Dependence of the composition of the solid phase on P_{CO_2}/P_{CO} in the gaseous phase in equilibrium with it

1104°K		1182°K	
Composition of the solid phase FeO (in mole %)	P_{CO_2}/P_{CO}	Composition of the solid phase FeO (in mole %)	P_{CO_2}/P_{CO}
1.008	0.53	0.95	0.47
1.032•	0.53	0.017•	0.47
1.047	0.58	1.042	0.51
1.057•	0.75	1.059•	0.79
1.075•	1.15	1.072•	1.05
1.089•	1.67	1.083	1.45
1.090	1.58	1.100•	2.12
1.092•	1.72	1.106•	2.51
1.096	1.95	1.107	2.85
1.097	2.01	1.116•	3.12
1.124	2.86	1.220	3.12
1.150•	2.86		

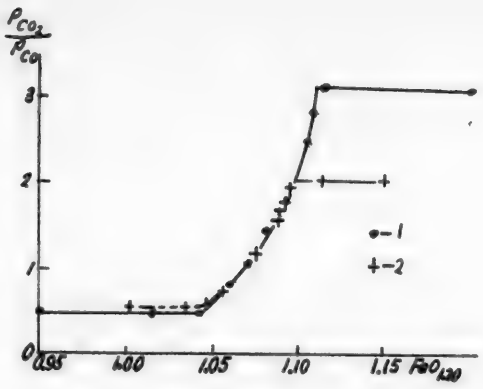

Fig. 1. Dependence of P_{CO_2}/P_{CO} on the composition of the solid phase. 1 – 1182°K; 2 – 1104°K.

Darken and Garri, having a significant dispersion of points, in view of the comparatively low precision of the experiments, constructed a straight line through them. Our data, which indicate the inapplicability of Henry's law in this case, appear to be considerably more natural.

That interval of composition of the solid phase in which the magnitude of the ratio P_{CO_2}/P_{CO} depends on the composition is taken by all authors as the region of homogeneity of ferrous oxide. Our data (Fig. 1) lead to a magnitude for the region of homogenity that is close to that found by other authors (Table 2).

TABLE 2

Author	Temp. (in °C)	Range in which ferrous oxide exists.
Darken and Garri [2] (extrapolation)	800	$FeO_{1.05} - FeO_{1.112}$
Jette and Foote [3]••	800	$FeO_{1.059} - FeO_{1.11}$
Matsubara [4]	863	$FeO_{1.055} - FeO_{1.127}$
Schenk [1]	800	$FeO_{1.04} - FeO_{1.12}$
Pfeil [5]	800	$FeO_{1.096}$
Our data	831	$FeO_{1.0435} - FeO_{1.0975}$
	909	$FeO_{1.0950} - FeO_{1.1075}$

The dependence of the equilibrium pressure of oxygen (O_2) on the composition of the solid phase is depicted in Figs. 2 and 3. The magnitudes of the equilibrium pressures of O_2 obtained from our data for the ratio P_{CO_2}/P_{CO} and the equilibrium constants for $CO_2 \rightleftarrows CO + \frac{1}{2} O_2$, were taken equal to $8.1 \cdot 10^{-17}$, for 1104°K and equal to $3.24 \cdot 10^{-16}$ [6] for 1182°K according to the formula:

$$P_{O_2} = K^2_{equilibrium}\left(\frac{P_{CO_2}}{P_{CO}}\right)^2 .$$

If, from the course of the isotherm P_{CO_2}/P_{CO} – composition of the solid phase, a completely determined and clear-cut representation of the position of the lower boundary of the region of homogeneity of ferrous oxide is found, it is impossible to say this concerning the isotherms: P_{O_2} – composition of the solid phase.

The fact is that all the isotherms (Figs. 1, 2, 3) converge asymptotically toward the straight line portion corresponding to the region of heterogeneity; it is, therefore, difficult to establish the lower boundary of the region of homogeneity. This is particularly noticeable in utilizing the isotherm: P_{O_2} – composition, since its points are obtained by squaring the values of the ratio P_{CO_2}/P_{CO}.

Thus, the lower boundary of the region of homogeneity of ferrous oxide must be considered as not completely reliably established either by us or by the preceding authors.

The results of the roentgenographic investigations of Jette and Foote can not be considered conclusive here, inasmuch as these authors took the roentgenograms at room temperature, when ferrous oxide is in general metastable. The possibility is not excluded that the region of homogeneity of ferrous oxide extends down to the

• These data refer to experiments in the course of which equilibrium was reached via reduction of the solid phase; the others – via oxidation.

•• The data of Jette and Foote were obtained in the course of X-ray investigations.

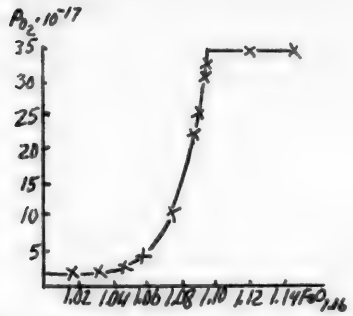

Fig. 2. Dependence of P_{O_2} (atm.) on the composition of the solid phase at 1104° K.

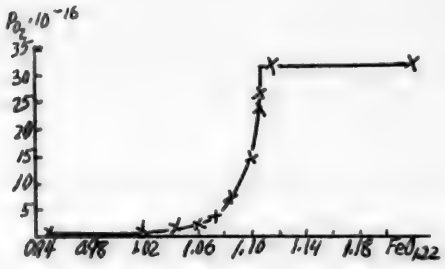

Fig. 3. Dependence of P_{O_2} (atm.) on the composition of the solid phase at 1182° K.

composition corresponding to the formula FeO. We propose to determine the lower boundary of the region of homogeneity, using phase analysis of determinations of magnetic susceptibility as the method.

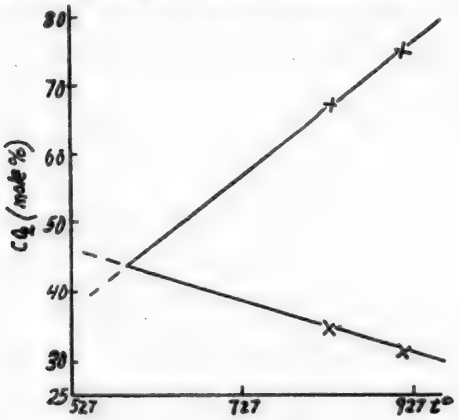

Fig. 4. Extrapolation of the equilibrium composition of the gas (corresponding to the upper and lower boundaries of the region of homogeneity of ferrous oxide) to the temperature at which this phase disappears.

The values found by us for the equilibrium composition of the gas (expressed in molecular percentages of CO_2), corresponding both to the upper and to the lower boundary of the region of homogeneity of ferrous oxide are shown in Figure 4.

Extrapolation of these data in an assumed linear dependence of P_{CO_2} on the temperature, leads to a temperature of disappearance of the wustite, equal to 591°C, which is close to the known value, found by experiment, of 572°C.

The Enthalpy of Formation and the Entropy of Ferrous Oxide of Various Compositions. At a temperature of 1104°K the lower boundary of the region in which ferrous oxide exists corresponds to a composition of $FeO_{1.0435}$, i.e., at 1104°K the phase with this composition is reduced to metallic iron as a result of reaction with the mixture CO_2/CO at a constant ratio (throughout the entire extent of the reduction process) of the partial pressures of these gases (we are here neglecting the portion corresponding to a solid solution of oxygen in iron—oxyferrite—since it can not introduce substantial error).

In conformity with this, the change in free energy corresponding to the process:

$$FeO_{1.0435} + 1.0435CO = Fe + 1.0435CO_2$$

at 1104°K, can be found by the generally-known formula:

$$\Delta F = -nRT \ln P_{CO_2}/P_{CO}.$$

At 1182°K the composition $FeO_{1.039}$ corresponds to the lower boundary of the region in which ferrous oxide exists, i.e., the change in free energy corresponding to the portion of the process:

$$FeO_{1.039} + 1.039CO = Fe + 1.039CO_2$$

can be found as in the preceding case.

As regards the portion of the process:

$$FeO_{1.0435} + 0.0045CO = FeO_{1.039} + 0.0045CO_2,$$

the change in free energy corresponding to it (at 1182°) can be found by the equation:

$$\Delta F = -RT \int_{x}^{x+n} \ln \frac{P_{CO_2}}{P_{CO}} dn,$$

since in this portion the process is completed at variable values of P_{CO_2}/P_{CO}. We were also obliged to find in similar fashion the values of the change in free energy corresponding to the other portions of the process:

$$FeO_{1+x+n} + nCO = FeO_{1+x} + nCO \qquad (a)$$

We performed the integration graphically. The magnitudes of the changes in free energy set down in Table 3 were found in this manner.

TABLE 3

Change in the composition of the solid phase	ΔF corresponding to the process (a) (in calories)	
	1104°K	1182°K
$FeO_{1.089} - FeO_{1.0435}$	—	+ 6.5
$FeO_{1.0435} - FeO_{1.05}$	+ 8.3	+ 9.0
$FeO_{1.05} - FeO_{1.06}$	+ 7.3	+ 8.0
$FeO_{1.06} - FeO_{1.07}$	+ 2.3	+ 2.5
$FeO_{1.07} - FeO_{1.08}$	− 2.9	− 3.1
$FeO_{1.08} - FeO_{1.09}$	− 8.0	− 8.6
$FeO_{1.09} - FeO_{1.0975}$	− 9.8	− 10.1

Calculation of the changes in enthalpy and entropy of the process under consideration was conducted by solving the system of equations

$$\Delta F_{1104} = \Delta H_{1104} - 1104\Delta S_{1104},$$

$$\Delta F_{1182} = \Delta H_{1104} + \Delta\Delta H - 1182(\Delta S_{1104} + \Delta\Delta S),$$

where quantities ΔΔH and ΔΔS – are auxiliary terms consisting of the changes, respectively, of ΔH and ΔS during the transition from 1140° to 1182°K. ΔΔH and ΔΔS were calculated on the basis of the values of the enthalpy of the conversion Feα–Feβ (165 cal), and Feβ–Feγ and the temperature dependence of the heat capacity of CO_2, CO, Fe, and ferrous oxide [6] (the latter was taken as independent of the composition.

$$CO_2: C_p = 10.34 + 2.74 \cdot 10^{-3}T - 1.955 \cdot 10^{5}T^{-2},$$
$$CO: C_p = 6.6 + 1.20 \cdot 10^{-3}T,$$
$$\text{"FeO"}\ C_p = 12.62 + 1.492 \cdot 10^{-3}T - 0.762 \cdot 10^{5}T^{-2},$$
$$Fe_\alpha\ C_p = 4.13 + 6.38 \cdot 10^{-3}T,$$
$$Fe_\beta\ C_p = 11.50 + 12 \cdot 10^{-3}T,$$
$$Fe_\gamma\ C_p = 7 + 4 \cdot 10^{-3}T,$$

according to the formulas:

$$\Delta\Delta H = \Delta aT + \frac{\Delta b}{2}(T_2^2 - T_1^2) + \Delta C\left(\frac{1}{T_2} - \frac{1}{T_1}\right), \quad \Delta\Delta S = \int_{T_1}^{T_2} \frac{\Delta C_p}{T}\, dT.$$

Thus, the values of the quantities $\Delta H_{1104°}$ and $\Delta S_{1104°}$ for all the processes set forth in Table 3 were found. The magnitudes of the changes in the enthalpy of the processes under consideration at 298°K were found by use of the same equations and the temperature dependence of the heat capacities of CO_2, CO, βFe, αFe, and FeO, and also of the magnitude of the enthalpy of the conversion of βFe into αFe (which occurs at 1050°K).

TABLE 4*

Composition of the solid phase	−ΔH of formation (in kcal.)	Composition of the solid phase	−ΔH of formation (in kcal.)
$FeO_{1.0435}$	65.973	$Fe_{0.9583}O$	63.231
$FeO_{1.05}$	66.439	$Fe_{0.9534}O$	63.2
$FeO_{1.06}$	67.159	$Fe_{0.9434}O$	63.360
$FeO_{1.07}$	67.877	$Fe_{0.9346}O$	63.447
$FeO_{1.08}$	68.594	$Fe_{0.9259}O$	63.510
$FeO_{1.09}$	69.310	$Fe_{0.9174}O$	63.585
$FeO_{1.0975}$	69.872	$Fe_{0.9112}O$	63.665

With the aid of these quantities and the values of the enthalpies of formation of CO_2 and CO (94.0 and 26.39 kcal respectively), the enthalpies of formation of ferrous oxides of various composition were calculated as set forth in Table 4. The dependence of the enthalpy of formation on the composition of the solid phase is presented graphically in Fig. 5. The entropy changes accompanying the process of gradual reduction of ferrous oxide by carbon monoxide are summarized in Table 5.

At 298°K the change in the entropy of the processes (3) – (6) should be less than that at 1104°K by 0.061 cal/1° (we found this quantity as

* We express the composition of ferrous oxide both as $Fe_{1-x}O$ and as FeO_{1+x}. The first method of transcription seems more correct from the point of view of the structure of this compound, but the second method is more widely employed.

$$\int_{298}^{1104} \frac{\Delta C_p}{T}\, dT,$$

assuming the heat capacity of $FeO_{1.06}$, $FeO_{1.05}$ and so forth, to be identical).

Thus, a reduction in the entropy of 0.06-0.05 cal./1° is associated with the processes (3) – (6) at standard temperature.

TABLE 5

Process	Change in the composition of the solid phase	ΔS in cal/1° (at 1104°)
1	$FeO_{1.0435} + 1.0435\ CO = Fe + 1.0435\ CO_2$	−4.924
2	$FeO_{1.05} + 0.0065\ CO = FeO_{1.0435} + 0.0065\ CO_2$	−0.0083
3	$FeO_{1.06} + 0.01\ CO = FeO_{1.05} + 0.01\ CO_2$	−0.011
4	$FeO_{1.07} + 0.01\ CO = FeO_{1.06} + 0.01\ CO_2$	−0.004
5	$FeO_{1.08} + 0.01\ CO = FeO_{1.07} + 0.01\ CO_2$	+ 0.0013
6	$FeO_{1.09} + 0.01\ CO = FeO_{1.08} + 0.01\ CO_2$	+ 0.006
7	$FeO_{1.0975} + 0.0075\ CO = FeO_{1.09} + 0.0075\ CO_2$	+ 0.0034

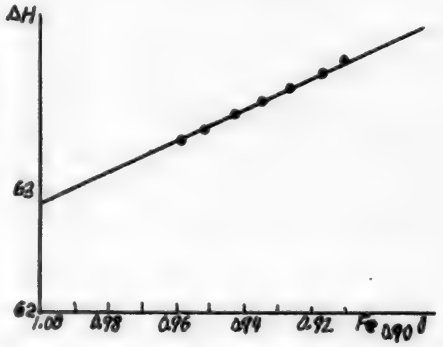

Fig. 5. D ependence of $\Delta H_{formation}$ (in kcal) on the composition of ferrous oxide.

At the same time

$$S_{FeO_{1.06}} - S_{FeO_{1.05}} = 0.01\,(S_{CO_2} - S_{CO}) + 0.06.$$

Using the values of the entropy at 298°K for CO_2 (51.08 cal./mole/1°) and CO (47.32 cal./mole/1°), we obtain as a result

$$S_{FeO_{1.06}} - S_{FeO_{1.05}} = 0.1 \text{ cal./mole/1°}.$$

In other words, the increase in the content of oxygen in ferrous oxide is accompanied byan increase in the entropy (calculating on 1 g-atom of iron). Even in calculating on 1 g-atom (both of iron and of oxygen) the entropy is also somewhat increased $\left(\text{by the quantity } \frac{S_{FeO_{1+x}}}{2+x}\right)$.

However, it is evident from Table 5 that this increase in entropy is somewhat retarded in proportion to the increase in oxygen content in the ferrous oxide. This appears to be the cause of the fact that the graph of the pressure of O_2 against the composition of the solid phase changes curvature and becomes more and more steep, which determines the break in the region of homogeneity of ferrous oxide on the side bordering on Fe_3O_4.

SUMMARY

1. The equilibrium of the process of the reduction of ferrous oxide by mixtures of CO_2/CO at temperatures of 1104 and 1182°K was investigated.

2. In the investigated temperature range, the equilibrium constant of the process $FeO_{1+x+y} + yCO \rightleftharpoons FeO_{1+x} + yCO_2$within the limits of the region of homogeneity of ferrous oxide, is practically independent of the temperature.

3. The upper limit of the region of homogeneity of ferrous oxide corresponds to a composition of $FeO_{1.0975}$ at 1104°K and of $FeO_{1.1075}$ at 1182°K.

4. It was established that the dependence of the equilibrium pressure of atomic oxygen on the composition of the solid phase did not obey Henry's law.

5. It was established that the entropy of ferrous oxide, calculated for 1 g-atom, is somewhat increased in proportion to the increase in the content of oxygen in this phase.

6. The magnitudes of the enthalpies of formation of ferrous oxide of various compositions at standard conditions (Table 4) were found. The magnitude of the enthalpy of formation of ferrous oxide appears to be a linear function of its composition.

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PHYSICO-CHEMICAL ANALYSIS OF THE SYSTEM:

ALUMINUM CHLORIDE – ACETAMIDE – WATER

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Acetamide as an addendum in complex formation reactions has been insufficiently studied.

B. N. Menshutkin [1, 2, 4], while investigating molecular compounds of the halides of several metals of the first and second main subgroups, established that compounds with acetamide form only those halides which crystallize from aqueous solutions in the form of hydrates; the molecular compounds with acetamide with any degree of strength yield almost no hydrates. According to the data of B. N. Menshutkin, compounds of magnesium halides with acetamide are stronger than compounds with alcohol, acetone and ether.

$NaBr \cdot 2CH_3CONH_2$ and $NaI \cdot 2CH_3CONH_2$ are described in the literature [2]. Attempts to obtain analogous compounds of sodium chloride and also of the potassium halides did not give positive results. The compound $KI \cdot 6CH_3CONH_2$ obtained by Walker and Jahnson [3] with a melting point of 59°, as was shown by B. N. Menshutkin [1], does not exist. Walker and Jahnson mistook a eutectic with the same melting point and composition for a compound.

On the other hand, there is a great analogy in the physico-chemical properties of water and acetamide. Acetamide, like water, possesses high dielectric properties. The dielectric constant of acetamide is 59.1 [5]. Mineral salts are quite soluble in fused acetamide and form solutions with acetamide which readily conduct an electric current. The investigations of Walker and Jahnson [3] of the electrical conductivity of solutions of certain mineral salts in acetamide demonstrated that the molecular conductivity was approximately identical for aqueous and acetamide solutions.

The cryoscopic investigations of acetamide solutions of mineral salts conducted by Bruni and Manuelli [6], showed that the salts are almost completely dissociated.

Aluminum chloride forms a hydrate with six molecules of water: $[Al(H_2O)_6]Cl_3$. Attempts to obtain a complex compound of aluminum chloride with acetamide by crystallization of aqueous, water-alcohol and hydrochloric acid solutions were not crowned with success.

The results of an investigation of complex formation of aluminum chloride with acetamide by the methods of physico-chemical analysis are presented in the present article.

EXPERIMENTAL

We determined the specific gravity, viscosity and electrical conductivity at 18, 25 and 35°, and also conducted cryoscopic investigations of the system: aluminum chloride – acetamide – water.

We used chemically pure aluminum chloride hexahydrate for the work. 43.63% chlorine was found in the preparation. The result obtained by calculation from the formula: $AlCl_3 \cdot 6H_2O$ is 44.07%. Acetamide was recrysallized from alcohol and dried at 50-60°. The melting point of the preparation obtained was 81°. The viscosity was determined with an Ostwald viscosimeter.

The solutions for the investigation were prepared by the method of isomolar concentrations proposed by Ostromyslensky [7]. 0.25 molar solutions of aluminum chloride and acetamide were mixed in various volume ratios at constant total volume.

The results of the measurements of specific gravity, viscosity and specific electrical conductivity are presented in Tables 1, 2, 3 and in Figs. 1 and 2.

The temperature coefficients of viscosity and electrical conductivity which are presented in Table 4 and Fig. 2 (curves 4 and IV) were calculated from the data obtained.

TABLE 1

The system: $AlCl_3$–CH_3CONH_2–H_2O
Temperature 18°

Molar percent of acetamide	d_4^{18}	Viscosity (in centipoises) $\eta \cdot 10^3$	Specific electrical conductivity $\kappa \cdot 10^3$ ohm^{-1} cm^{-1}
0	1.0269	1290.5	42.5
33.3	1.0186	1226.1	30.6
50	1.0135	1189.2	23.9
66.7	1.0094	1160.0	17.1
75	1.0072	1146.8	13.3
80	1.0049	1132.0	11.0
85.7	1.0035	1122.0	8.2
91.7	–	–	5.3
100	1.0001	1098.6	0.22

TABLE 2

The system: $AlCl_3$–CH_3CONH_2–H_2O
Temperature 25°

Molar percent of acetamide	d_4^{25}	Viscosity (in centipoises). $\eta \cdot 10^3$	Specific electrical conductivity $\kappa \cdot 10^3$ ohm^{-1} cm^{-1}
0	1.0254	1084.9	48.9
33.3	1.0161	1028.1	34.9
50	1.0119	998.6	27.4
66.7	1.0072	975.1	19.8
75	1.0053	960.5	15.4
80	1.0034	948.8	12.6
85.7	1.0020	939.9	9.8
91.7	–	–	6.0
100	0.9980	919.0	0.25

TABLE 3

The system: $AlCl_3$–CH_3CONH_2–H_2O
Temperature 35°

Molar percent of acetamide	d_4^{35}	Viscosity (in centipoises). $\eta \cdot 10^3$	Specific electrical conductivity $\kappa \cdot 10^3$ ohm^{-1} cm^{-1}
0	1.0226	879.5	58.0
33.3	1.0134	837.0	41.6
50	1.0088	817.4	31.6
66.7	1.0040	795.4	23.8
75	1.0021	780.3	18.6
80	1.0002	775.0	15.3
85.7	0.9989	768.0	11.5
91.7	–	–	7.3
100	0.9951	749.3	0.30

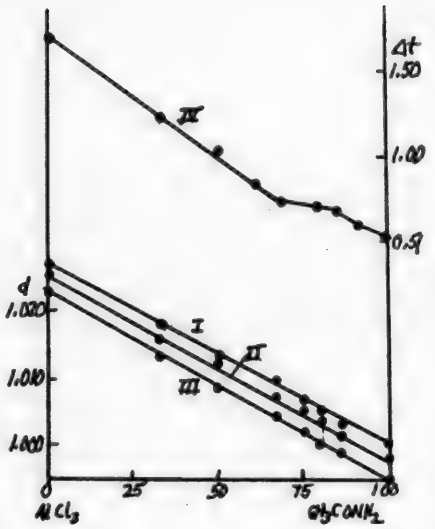

Fig. 1. The system: $AlCl_3$–CH_3CONH_2–H_2O. Specific gravity: I – 18°; II – 25°; III – 35°; IV – temperature depression.

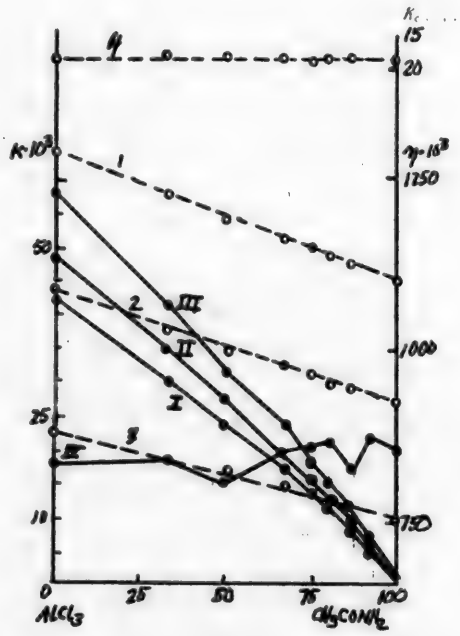

Fig. 2. The system: $AlCl_3$–CH_3CONH_2–H_2O. Specific electrical conductivity: I – 18°; II – 25°; III – 35°; IV – temperature coefficient of electrical conductivity. Viscosity: 1 – 18°; 2 – 25°; 3 – 35°; 4 – temperature coefficient of viscosity.

Cryoscopic investigations of the system were conducted in a Beckmann apparatus. Solutions containing considerable quantities of acetamide crystallized with difficulty. To avoid considerable supercooling, we were compelled to elicit crystallization by the addition of a primer—small ice crystals. The results of the measurements of the temperature depression of the system are shown in Table 5 and Fig. 1, Curve IV.

TABLE 4

The system: $AlCl_3$–CH_3CONH_2–H_2O
Temperature coefficients of viscosity and electrical conductivity

Molar percent of acetamide	Temperature coefficient	
	Viscosity	Electrical conductivity
0	−0.0187	0.0186
33.3	−0.0183	0.0192
50	−0.0184	0.0153
66.7	−0.0185	0.0202
75	−0.0188	0.0208
80	−0.0186	0.0214
85.7	−0.0186	0.0173
91.7	–	0.0217
100	−0.0187	0.0200

TABLE 5

Cryoscopy of the system: $AlCl_3$–CH_3CONH_2–H_2O

Molar percent of acetamide	Temperature depression Δt (in degrees)
0	1.72
33.3	1.23
50	1.04
66.7	0.85
75	0.74
80	0.71
85.7	0.68
91.7	0.61
100	0.52

The temperature depression of a 0.25 molar solution of aluminum chloride amounted to 1.72° according to our data. The apparent degree of dissociation of aluminum chloride calculated according to the formula $a = \frac{\Delta t' - \Delta t}{\Delta t(m-1)}$ was equal to 0.88. The lowering of the freezing point of a 0.25 molar acetamide solution amounted to 0.52°. The molecular weight of acetamide calculated according to these data was 53.5, according to the formula CH_3CONH_2 – 59. The reduction in the molecular weight of acetamide was probably associated with partial hydrolysis of acetamide proceeding according to the scheme:

$$CH_3CONH_2 + 2H_2O \rightleftharpoons CH_3COOH + NH_4OH.$$

The degree of hydrolysis can be calculated by the same formula, taking $\underline{m} = 2$. The degree of hydrolysis calculated in that way is equal to 0.13.

Discussion of Results

As is evident from Figs. 1 and 2, the specific gravity and viscosity of the system was found to be a linear function of the concentration of acetamide. The temperature coefficient of viscosity (Fig. 2) has the same value for all compositions of the system.

The isotherms of specific gravity and viscosity did not give any indications of chemical reaction of the components of the system. The isotherms of specific electrical conductivity (Fig. 2) deviate from rectilinearity, giving some deflection at 50% acetamide and a particularly sharp deflection at 85.7% acetamide which corresponds to a molar ratio of aluminum chloride to acetamide of 1:6.

The temperature coefficient of electrical conductivity (Fig. 2) forms two minimums at the very points corresponding to compositions of 1:1 and 1:6.

The temperature depression of the system (Fig. 1) is diminished irregularly in proportion to the increase in the concentration of acetamide. As a consequence of the dissociation of aluminum chloride, which proceeded to a greater extent than the hydrolysis of acetamide, the concentration of particles in the solution did not remain constant, but diminished in proportion to the increase in acetamide, at the beginning very sharply, and then was retarded, which was reflected in the course of the curve of the dependence of the temperature depression on the composition of the system. However, in the region of acetamide concentration of 85.7% (molar ratio 1:6) there is some slope of a section after which a rectilinear diminishing of the depression sets in, which, probably, is associated with a weak chemical reaction in the system.

Thus, only the isotherms of electrical conductivity and cryoscopic measurements give any indication of a chemical process proceeding in the system.

According to Kurnakov [8], viscosimetry is a more sensitive method of physico-chemical analysis than electrical conductivity measurements. However, the isotherms of viscosity of the given system do not have any singular points, in contrast to the electrical conductivity isotherms. But this character of linear dependence of the viscosity of a mixture of two solutions on the composition is itself, to a certain extent, anomalous. The viscosity of an ideal mixture is not linearly dependent on the composition [9], but has a hyperbolic character. The linear dependence of the viscosity in our system can be explained by analogy with the physico-chemical properties of water and acetamide. Among the other factors determining the viscosity of a substance, the intermolecular forces have an essential significance. As a consequence of the great similarity in the physico-chemical properties of water and acetamide, substitution of water molecules for acetamide molecules does not substantially change the molecular reactive forces, and, therefore, is not reflected in the viscosity of the system.

It is usually considered that metallic ions with the electron shell of an inert gas form complex compounds primarily at the expense of electrostatic forces [10]; at the same time, an important role is played, on the one hand, by the charge of the metallic ion and its radius, and on the other hand, by the magnitude of the permanent dipole of the addendum. The polarization forces play a secondary role [11]. The permanent dipole moment of acetamide, according to the data of Bates and Hobbs [12], is equal to 3.44 D, i.e., approximately 2 times greater than the dipole moment of water. Nevertheless, acetamide does not form stable complex compounds with aluminum halides in aqueous solution. The formation of molecular compounds as a result of an ion dipole reaction is characteristic of the alkaline and the alkaline earth metals. Aluminum, possessing a high ionization potential and a small electron affinity, primarily forms covalent bonds. In aqueous solution the hydrated ion of aluminum preserves the octahedral structure characteristic of the crystallohydrate $[Al(H_2O)_6]Cl_3$ [13], in which 6 molecules of water are bound covalently to the aluminum ion. The aluminum ion can be hydrated by a large number of water molecules, but the part of the water molecule forming the last shell is bound with the ion $[Al(H_2O)_6]^{\cdots}$ by electrostatic bonds. Starting with these concepts, we can assume that stable water-soluble compounds can be formed only with addenda having the capacity to form a more covalent bond with the aluminum ion than the $Al{-}OH_2$* bond, or if the bond is strengthened by ring formation.

Acetamide, although it contains trivalent nitrogen, can not form a more covalent bond, since the donor property of nitrogen is greatly weakened by the presence of the carbonyl group. As was shown by Chernyaev and Nazarova [14], acetamide does not form the usual type of complex compound with divalent platinum salts. The substance obtained by them of the composition $Pt(NHCOCH_3)_2 \cdot H_2O$ (diacetimideplatinum) is, according to its character, an internal-complex compound. In this compound platinum forms a valent bond with nitrogen at the expense of the hydrogen of the amide group.

Aluminum forms internal-complex compounds stable in aqueous solution primarily with organic substances possessing acidic properties. The acidic function of acetamide is very weakly expressed. The dissociation constant of acetamide as an acid is equal to $8 \cdot 10^{-16}$ [15]. Taking into account the weakly basic property of aluminum hydroxide, the possibility of formation of internal-complex compounds of the aluminum ion with acetamide at the expense of the valent bond with the nitrogen of the amide group is improbable. This causes the instability of acetamide complexes of aluminum halides in aqueous solution.

SUMMARY

1. The specific gravity, viscosity and electrical conductivity of the system: aluminum chloride – acetamide – water at 18, 25 and 35° was measured by the method of isomolar concentrations.

2. The specific gravity and viscosity were found to be linearly dependent on the composition of the system. The isotherms of the specific electrical conductivity had a bend at a molar ratio $AlCl_3 : CH_3CONH_2$ equal to 1:1 and 1:6.

3. The temperature coefficient of viscosity has a constant value and does not depend on the concentration of acetamide in the system. The temperature coefficient of specific electrical conductivity has two minima, which correspond to molar ratios of 1:1 and 1:6.

4. The temperature depression of the system diminishes with increase in the concentration of acetamide. In the region of acetamide concentration corresponding to a molar ratio $AlCl_3 : CH_3CONH_2 = 1:6$, the fall in the depression is retarded and the curve Δt – composition in this region has a rather inclined section.

* The instability in aqueous solution of aluminum ammoniates is evidently exclusively associated with the low solubility of aluminum hydroxide.

5. The apparent degree of dissociation of aluminum chloride as a tetraionic electrolyte calculated from cyroscopic data amounts to 0.88. The molecular weight of acetamide in 0.25 molar solution was found to be equal to 53.5.

6. The instability of the acetamide complex of aluminum chloride in aqueous solution was explained by weakening of the donor properties of the nitrogen of the amide group, by the presence of the carbonyl group and the impossibility of formation of compounds of the internal-complex type, in view of the weakness of the acidic properties of acetamide.

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• See Consultants Bureau Translation, page 239.

PHYSICO-CHEMICAL INVESTIGATION OF THE REACTION OF TITANIUM TETRACHLORIDE WITH ETHYL ACETATE

Yu. A. Lysenko and O. A. Osipov

In the preceding articles [1, 2] we have shown that in systems composed of titanium tetrachloride and esters of monobasic acids, rather stable molecular compounds are formed in the liquid phase; at the same time, a complex of the composition $TiCl_4 \cdot E$ (where E = a molecule of ester) is more characteristic of titanium tetrachloride, in contrast to stannic tetrachloride which reacts with two molecules of ester. We attempted to explain this fact on the basis of the difference in the magnitudes of the tetrahedral covalent radii of titanium and tin. Investigation of a number of properties (viscosity, density, electrical conductivity) of the system was undertaken with the goal of obtaining further experimental basis for the earlier expressed hypothesis.

EXPERIMENTAL AND DISCUSSION OF RESULTS

We used c.p. titanium tetrachloride and ethyl acetate for the investigation. The latter was dried for a long time over calcium chloride after which it was twice redistilled. The fraction with a b.p. 77.1-77.8°; $d_D^{19.2}$ 0.8998; $n_D^{19.2}$ 1.3722 was used.

The methods for preparing the solutions and measuring the density, viscosity and electrical conductivity have been described previously [1]. The system was investigated at temperatures of 97 and 102°. The outer temperature limits were determined on the one hand by the rapid formation of crystals below 97°; on the other hand, by the circumstance that at temperatures above 102-105° change in the color of the melt from light yellow to brown began, which evidently is associated with partial resinification. The change in color was the more intense, the richer the melt in titanium tetrachloride.

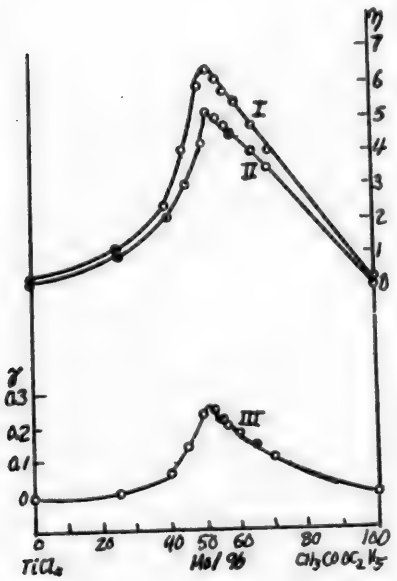

Fig. 1. Isotherms of viscosity. I – 97°; II – 102°; III – absolute temperature coefficient of viscosity.

In Fig. 1 (I and II) the results of the measurements of viscosity, expressed in centiposes for the two temperatures • are presented.

The viscosity isotherms, as is evident, pass through a pronounced maximum corresponding to 53 mole % of ethylacetate,, i.e., it is somewaht deflected to the side from the unit ratio of the components of 1:1. On the basis of the form of the viscosity isotherm one can definitely conclude that in the system: titanium tetrachloride – ethyl acetate, a molecular compound of the composition $TiCl_4 \cdot CH_3COOC_2H_5$ is formed in the liquid phase.

The pronounced maxima on the viscosity isotherms at 97 and 102° indicate the considerable thermal stability of the complex obtained. At 97° the viscosity maximum is 17.4 times greater than the viscosity of the most viscous component, and at 102° it is 14.8 times greater. It should be noted that, while the branch of the viscosity isotherm adjacent to the titanium tetrachloride is convex toward the composition axis for its entire extent, the branch adjacent to the ester is a straight line (and even somewhat convex toward the composition axis at 102°). This fact is evidence of the absence of chemical reaction between titanium tetrachloride and the molecular compound obtained.

• The data for 100% $CH_3COOC_2H_5$ are taken from [4].

The results of the calculation of the absolute temperature coefficient of viscosity are set forth in Fig. 1, III. The curve of the temperature coefficient as a function of the composition passes through a maximum corresponding to an almost equimolecular ratio of the components, and consequently, also confirms the existence of the compound $TiCl_4 \cdot CH_3COOC_2H_5$.

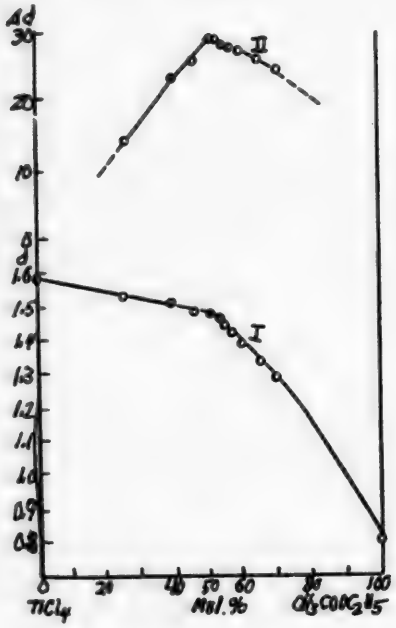

Fig. 2. Density isotherms of the binary system. Explanation in the text.

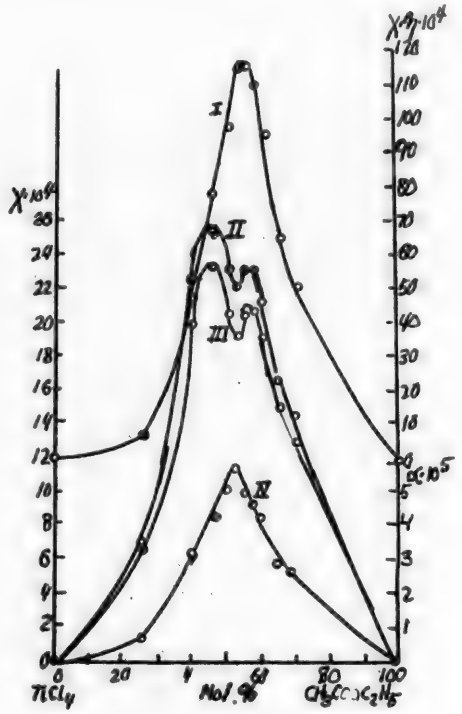

Fig. 3. Electrical conductivity isotherms of the binary system. Explanation in the text.

The results of the measurements of density at 102° are presented in Fig. 2, I. Here we do not cite an isotherm at 97° since it almost coincides with the isotherm at 102°, due to the low temperature coefficient.

Numerous experimental data indicate that the density of the system is not so characteristic a property as, for example, the viscosity, which serves to establish the presence of a chemical reaction between the components and to determine the composition of the compound obtained. However, the over-all form of the density diagram will indicate the condensation in the system which can be a result of chemical reaction between the components. As is evident from Fig. 2, significant condensation occurs in our system, particularly in the region of 45-55 mole % of ethyl acetate. Such a great condensation of the system can be explained only by a pronounced chemical reaction between the components, with the formation of a compound of the composition $TiCl_4 \cdot CH_3COOC_2H_5$. If we plot the numerical value of the deviation of the experimental density isotherm from the additive straight line along the ordinate axis, and the composition along the abscissa, then we obtain a curve (Fig. 2, II), the maximum of which corresponds to the composition of the compound.

The data of the measurements of electrical conductivity of the system are presented in Fig. 3.

The conductivity isotherms consist of curves having two maxima and one pronounced minimum corresponding to 53 mole % of ethyl acetate [Fig. 3, II and III).

According to the character of the conductivity curves, our system is formed from nonconducting components which, chemically reacting, yield a compound that can conduct a current [3].

In Fig. 3 (I and IV) are also set forth the curves of the absolute temperature coefficient and the reduced electrical conductivity. Both curves pass through sharp maxima, corresponding to the composition of the compound.

SUMMARY

1. The viscosity, density and electrical conductivity of the system: titanium tetrachloride—ethyl acetate, at temperatures of 97 and 102° were measured.

2. It was shown that titanium tetrachloride forms a molecular compound of the composition $TiCl_4 \cdot CH_3COOC_2H_5$ with ethyl acetate, in contrast to stannic tetrachloride, which reacts with two molecules of the ester.

3. It was shown that the results of our investigations of the composition ratio of the obtained compound confirm the earlier expressed hypothesis.

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KINETICS OF THE AQUATIZATION OF UREA COMPLEXES OF CHROMIUM

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One of the peculiarities of complex compounds of trivalent chromium is that they are formed and decomposed rather slowly in aqueous solutions. In contrast to the other elements of the fourth period of the Mendeleev periodic table, which form complexes(along with slowly reacting complexes), that are decomposed instantly, all the complex compounds of chromium which have been studied are decomposed with measureable speed [1].

The exchange kinetics of complexly bound water in ions of the type $M(H_2O)_6^{3+}$ (M=Al, Fe, Co, Ga, Cr) was recently studied by the method of labeled atoms; it was shown that only in the case of the hexahydrate of the chromium ion does the water exchange process proceed with measureable speed [1]; in all the other cases the equilibrium state was reached instantly.

The rather high stability of the very numerous complex compounds of chromium in aqueous solutions is evidently to be explained by the slowness of aquatization (substitution of water molecules in the internal spheres of the addenda). The circumstance that the overwhelming majority of the complexes of trivalent chromium can not be obtained by the direct route in aqueous solution argues in favor of this hypothesis.

The preparative aspects of the complex hexaurea chromium salt havebeen studied rather thoroughly [3, 4]. These salts can not be obtained via simple mixture of the constituent parts in aqueous solution. If these salts are obtained by evaporating the solution to dryness, then the ion $[Cr(CON_2H_4)_6]^{3+}$ can be detected in the solution for a rather prolonged time.

The first attempt to study the kinetics of the aquatization of hexaurea chromium salts was made by Kilpatrik [4]. This author studied the rate of the reaction at only one temperature (22.5°), and arbitrarily assumed the complete substitution of urea molecules by water according to the scheme:

$$[Cr(CON_2H_4)_6]^{3+} + 6H_2O = [Cr(H_2O)_6]^{3+} + 6CON_2H_4.$$

To enumerate the activation energy and the preexponential factor it was necessary to study the rate of this reaction at several temperatures. The assumption concerning complete displacement of urea molecules from the inner sphere appeared baseless to us and required additional testing.

EXPERIMENTAL

As starting substance hexaurea chromic chloride $[Cr(CON_2H_4)_6]Cl_3$, was synthesized and purified by the method of Pfeiffer [5]. The purity of the preparation obtained was controlled by analysis for chromium content.

TABLE 1

Rate Constants of the Aquatization Reaction of the Hexaurea Chromic Ion at 30°

Time (in minutes	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})
0	23.95	–	47.13	–	70.82	–
720	18.09	3.90	36.43	3.58	54.52	3.63
1440	13.50	3.98	27.36	3.78	41.27	3.75
2160	10.09	4.00	19.87	4.00	30.06	3.88
2880	8.31	3.68	15.54	3.85	23.18	3.88
3600	6.62	3.57	11.87	3.83	17.07	3.95
4320	4.33	3.96	8.41	3.99	12.74	3.97
Mean value	–	3.85	–	3.84	–	3.84

Mean value K = $3.84 \cdot 10^{-4}$ minutes^{-1}.

TABLE 2

Rate constants of the aquatization reaction of the hexaurea chromic ion at 40°

Time (in minutes)	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})
0	47.14	–	45.40	–
120	38.46	17.0	–	–
240	33.00	14.9	30.76	16.2
360	26.05	16.5	–	–
480	22.33	15.6	21.09	16.0
600	18.36	15.7	–	–
720	13.13	15.8	14.64	15.7
840	–	–	10.67	17.2
960	–	–	8.44	17.5
Mean value	–	15.9	–	16.5

Mean value K $1.62 \cdot 10^{-2}$ minutes^{-1}.

In contrast to the method used by Kilpatrik [4], the content of $[Cr(CON_2H_4)_6]^{3+}$ in the solution was determined by a volumetric method proposed by us. The essence of this method consisted of adding to the solution under investigation an excess of a titrated solution of $K_4Fe(CN)_6$. The complex ion then precipitated quantitatively in the form of the salt $[Cr(CON_2H_4)_6]_4[Fe(CN)_6]_3$; the product of the aquatization of the ferrocyanide salt did not precipitate. The excess ferrocyanide was determined by titration with permanganate.

A determined weighed portion of hexaurea chromic chloride was dissolved in water and the solution obtained was stirred in an ultrathermostat in which constant temperature was maintained with a variation of ± 0.05°. After a determined interval of

TABLE 3

Rate constants of the aquatization reaction of the hexaurea chromic ion at 50°

Time (in minutes)	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})
0	22.38	–	47.07	–	71.12	–	95.85	–
120	9.37	72.5	19.26	74.5	–	–	36.80	79.7
180	6.18	71.5	13.69	68.7	18.96	74.0	27.39	69.6
240	4.48	67.0	9.67	66.0	12.77	72.0	17.12	71.8
300	2.98	67.2	6.59	65.5	8.15	72.5	13.69	64.8
360	1.49	75.2	4.28	67.2	5.70	70.4	8.56	67.1
Mean value	–	70.7	–	68.4	–	72.2	–	70.7

Mean value K $7.06 \cdot 10^{-2}$ minutes^{-1}.

TABLE 4

Rate constants of the aquatization reaction of the hexaurea chromic ion at 60°

Time (in minutes	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})	Concentration of the salt · 10^3 (in mole/liter)	Rate constant · 10^4 (in minutes^{-1})
0	23.05	–	46.72	–	69.45	–
30	11.05	24.5	21.47	25.9	34.10	23.7
60	5.37	24.3	11.68	23.1	15.47	25.0
90	2.53	24.6	6.00	22.8	7.89	24.2
120	1.26	24.2	1.89	25.7	3.16	25.8
Mean value	–	24.4	–	24.4	–	23.7

Mean value K $2.45 \cdot 10^{-2}$ minutes^{-1}.

time, samples of the solution were removed and the hexaurea chromic ions were at once precipitated with excess titrated solution of potassium ferrocyanide. After 30 minutes the precipitate was filtered through a dry filter and a determined volume of the filtrate was titrated with permanganate solution. On the basis of these data the

concentration of the hexaurea chromic ions in the solution was calculated. A summary of the results obtained is set forth in Tables 1, 2, 3 and 4.

The rate constants were enumerated in all cases from the equation for monomolecular reactions. The values obtained for the rate constants are summarized in the same tables.

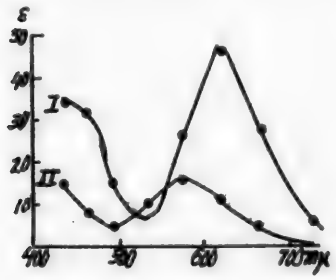

Fig. 1. Absorption spectra of aqueous solutions of hexaurea chromic salts (I) and the products of aquatization (II). Explanation in the text.

The optical characteristics of the solutions under investigation were subsequently studied on a universal photometer FM-2. The absorption spectrum of a freshly-prepared solution of hexaurea chromic chloride is set forth in Fig. 1.

In the course of time, the absorption spectrum of the solution changes in dependence on the temperature and with greater or less speed approaches to a fixed limit. The absorption spectrum of a solution containing the products of the aquatization of hexaurea chromic chloride, which does not change with time, is summarized in the same Fig. 1. This absorption spectrum is different from the absorption spectrum of aqueous solutions of chromic chloride.

The data presented show that during the decomposition of hexaurea chromic chloride the optical density changes most strongly in the wave length intervals 600-680 and 440-480 mμ. This circumstance was utilized by us in the study of the rate of aquatization of hexaurea chromic salts in aqueous solution.

Samples were taken from the solutions of hexaurea chromic salts mixed in the ultrathermostat after a fixed interval of time and poured into ice water. The samples removed together with the added ice water were reduced to determined volume and the optical density of the solutions was measured on a FM-2 photometer with filters with an effective wave length of 465, 619 and 665 mμ. The measurements were conducted at two temperatures (40 and 50°), and the initial concentration of the solutions was 0.04 and 0.05 molar. The results obtained are summarized in Tables 5 and 6.

TABLE 5

Rate constants of the aquatization reaction of the hexaurea chromic ion found by the optical method at 40° (Initial concentration of hexaurea chromic salt 0.05 molar)

Time (in minutes)	Light filter with λ = 665 mμ			Light filter with λ = 619 mμ			Light filter with λ = 465 mμ		
	D	$1-a$	10^3 K	D	$1-a$	10^3 K	D	$1-a$	10^3 K
0	1.32	1.000	–	2.32	1.000	–	1.57	1.000	–
120	1.19	0.881	1.06	2.15	0.901	0.87	1.43	0.880	1.08
240	1.10	0.798	0.94	1.96	0.791	0.98	1.32	0.786	1.00
360	0.99	0.697	1.00	1.76	0.675	1.09	1.20	0.684	1.05
480	0.90	0.615	1.01	1.62	0.594	1.08	1.10	0.598	1.07
600	0.82	0.541	1.03	1.50	0.523	1.08	1.03	0.538	1.04
720	0.77	0.495	0.98	1.40	0.471	1.05	0.99	0.496	0.96
∞	0.23	0.000	–	0.60	0.000	–	0.40	0.000	–

Mean value K $1.02 \cdot 10^{-3}$ minutes^{-1}.

Note. In Tables 5 and 6, D denotes the optical density, $1-a$ denotes the portion of unreacted salt, and K denotes the rate constant.

If we denote by D_1, D_2 and D respectively the initial, final and intermediate optical density and by $1-a$ the portion of the salt remaining unchanged, then we obtain the following relationship:

$$D = D_1(1-a) + D_2 a. \qquad (1)$$

From this the amount of salt remaining at any moment can be calculated according to the equation:

$$1-a = \frac{D-D_2}{D_1-D_2}, \qquad (2)$$

and the rate constant from the equation for monomolecular reactions:

$$K = \frac{2.303}{t} \log (1 - a). \qquad (3)$$

The values of the rate constants enumerated in this manner, are summarized in the same Tables 5 and 6.

TABLE 6

Rate constants of the aquatization reaction of the hexaurea chromic ion, found by the optical method at 50° (Initial concentration of hexaurea chromic salt 0.041 molar)

Time (in minutes)	Light filter with λ = 665 mμ			Light filter with λ = 465 mμ		
	D	1 − a	10^3 K	D	1 − a	10^3 K
0	1.10	1.000	–	1.30	1.000	–
120	0.73	0.594	4.33	0.89	0.577	4.60
180	0.58	0.429	4.71	0.75	0.433	4.65
240	0.48	0.319	4.75	0.64	0.320	4.73
300	0.40	0.231	4.88	0.55	0.227	4.94
	0.190	0.000	–	0.33	0.000	–
Mean value	–	–	4.67	–	–	4.73

Mean value K $4.70 \cdot 10^{-3}$ minutes^{-1}.

It was indicated above that the absorption spectrum of a solution containing the end products of the aquatization of chromic salts is different from the absorption spectrum of an aqueous solution of chromic chloride. The absorption spectrum of solutions of chromic salts slowly changes during the addition of urea to them. Consequently, in the equilibrium state in a solution containing complex compounds of chromium and urea, their composition will differ from that of the hexaurea chromic ion. This compound is not precipitated by ferrocyanide and is different in its absorption spectrum from hexaurea chromic salts.

In order to establish the composition of the compound being formed at the attainment of equilibrium, we utilized the method of Ostromyslensky-Zhob. Solutions of chromic chloride and urea of identical molarity (0.038 and 0.38 molar) were mixed in various ratios; after the passage of three days the optical density of the solutions was measured with light filters with effective wave lengths of 436 and 465 mμ. Preliminary experiments established that the optical density of the solutions under investigation reached fixed values and did not substantially change further. The results of the experiments are summarized in Table 7.

TABLE 7

Optical density of solutions containing $CrCl_3$ and urea

Ratio of the number of moles of $CrCl_3$ to CON_2H_4	Optical density		Discrepancy in the values for the optical density
	Found	Calculated	
1:9	0.31	0.29	0.02
2:8	0.61	0.58	0.03
3:7	0.85	0.87	−0.02
4:6	1.11	1.16	−0.05
5:5	1.35	1.45	−0.10
6:4	1.55	1.74	−0.19
7:3	1.95	2.03	−0.08
8:2	2.24	2.32	−0.08
9:1	2.48	2.61	−0.13

The optical density in the assumed absence of reaction between the chromic salts and urea was calculated for all the solutions investigated and the magnitudes of the discrepancies of the measured optical density from that theoretically calculated were found. The values of the discrepancies are summarized in the same Table 7; the maximum discrepancy in both cases was observed between ratios of the number of moles of Cr : CON_2H_4 1:1 and 1.5:1. Evidently a compound of the type $[Cr(CON_2H_4)(H_2O)_5]^{3+}$ is formed at the moment of achieving equilibrium in the system.

DISCUSSION OF RESULTS

The data set forth in Tables 1-6 are evidence of the fact that the values of the rate constant calculated in the assumed applicability to the aquatization reaction of hexaurea chromic ion of the equation for first order reactions, maintain a very satisfactory constancy.

The difference in the values of the rate constant calculated on the basis of the study of the optical density measurements at the time of, and according to the results of titration is worthy of attention. The constants obtained from the optical data remain approximately constant, but they are approximately 1.6 times less in absolute value than those found as a result of the chemical analysis of the solution.

This sort of decomposition can be explained if we assume that the aquatization process of the hexaurea chromic salts occurs in several stages:

$$I - [Cr(CON_2H_4)_6]^{3+} + H_2O = [Cr(CON_2H_4)_5 \cdot H_2O]^{3+} + CON_2H_4,$$

$$II - [Cr(CON_2H_4)_5 \cdot H_2O]^{3+} + H_2O = [Cr(CON_2H_4)_4 \cdot (H_2O)_2]^{3+} + CON_2H_4$$

and finally

$$V - [Cr(CON_2H_4)_2 \cdot (H_2O)_4]^{3+} + H_2O = [Cr(CON_2H_4)(H_2O)_5]^{3+} + CON_2H_4.$$

Ions of the $[Cr(CON_2H_4)_n(H_2O)_{6-n}]^{3+}_{(n<6)}$ type are evidently not precipitated by ferrocyanide.

The rate constant obtained by determination of the content of hexaurea chromic salt in the solution vai titration appears to be the rate constant of the first stage of aquatization of the complex salt.

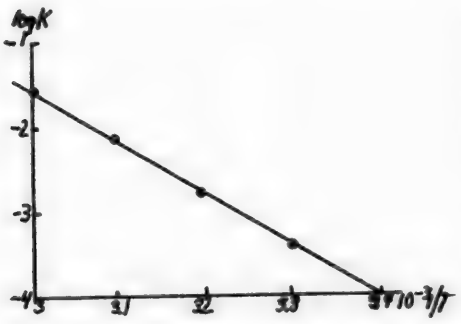

Fig. 2. Dependence of the rate constants of the aquatization reaction on the temperature.

Further displacement by water molecules of urea molecules from the inner sphere should lead to a certain change in the optical density of the solution. Consequently, the values of the rate constants obtained from the optical data, reflect not only the first stage of aquatization of the complex, but also the subsequent stages of this process.

The hypothesis of Kilpatrik concerning complete dislodgement from the inner sphere of urea molecules by water molecules was not substantiated. The aquatization process proceeds in stages and even in the moment of achieving equilibrium, complex ions remain in the solution.

The data obtained by the method of Ostromyslensky-Zhob indicate that the hypothetical composition of the complex appears to be a final product of the decomposition of $[Cr(CON_2H_4)(H_2O)_5]^{3+}$. This compound can be obtained both by destruction of the hexaurea chromic ion by water and by stirring solutions of chromic salt with urea.

Analysis of the temperature dependence of the rate constant of the reactions studied shows that in the given case the Arrhenius equation is rather strictly observed (Fig. 2).

The activation energy at the same time amounts to 13,200 kcal, while log pz = 16.45. The high value of the preexponential factor – pz attracts attention. Such a high value of the preexponential factor for ionic reactions proceeding in aqueous solutions has been observed previously [6]; Bjerrum [7] considered that the high value of the preexponential factor is a peculiarity of the complex formation reactions of numerous ions.

There is no single accepted opinion at the present time regarding the problem of the causes of such a high value for the pz factor.

Using the Arrhenius equation with the obtained constants, we calculated the rate constant of the aquatization of hexaurea chromic ion in aqueous solution for 22.5° and found $1.12 \cdot 10^{-4}$ min^{-1}, Kilpatrik found $1.11 \cdot 10^{-4}$ [5]. Thus, an entirely satisfactory agreement is observed between our data and the value for the constant (for another temperature) obtained previously.

SUMMARY

1. The rate constants of the aquatization reaction of the hexaurea chromic ion in aqueous solution at temperatures of 30, 40, 50 and 60° were measured and shown to be respectively equal to $3.84 \cdot 10^{-4}$, $1.62 \cdot 10^{-3}$, $7.08 \cdot 10^{-3}$ and $2.45 \cdot 10^{-2}$ minutes^{-1}. The activation energy (13,200 kcal) and log pz (16.45) were calculated.

2. The rate of the aquatization reaction of the hexaurea chromic ion was also studied by optical methods. The values obtained for the rate constant maintained a satisfactory constancy, but differed somewhat from those set forth above.

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DETERMINATION OF THE COMPOSITION AND THE INSTABILITY CONSTANTS OF COMPLEX COMPOUNDS BETWEEN METALS AND THIOUREA BY A POLAROGRAPHIC METHOD. II

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In a preceding communication [1] the question was raised as to whether the following sequence of the divalent metal series is maintained with regard to diminishing stability of the thiourea complexes:

$$Hg^{2+} > Cd^{2+} > Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+},$$

as could be expected from consideration of the changes in the covalency in the reactions of complex formation according to the data of Yatsimirsky [2], and as actually takes place for thiosulfate, halide and thiocyanate complexes. Dimensions were given there which characterize the structure and the stability of the thiourea complexes of two members of the above-mentioned series – lead and cadmium. The structure and the stability of the complexes of Zn, Ni, and Bi are considered in the present communication.

According to the data of A. T. Pilipenko and G. S. Lisetskaya [3], the instability constant of the thiourea complex of divalent mercury is equal to 10^{-28} (determined potentiometrically). The complex of divalent copper with thiourea does not exist, since the monovalent ion forms a complex, and therefore copper is excluded from the above-mentioned series. Measurement of the half-wave potentials was conducted under the same conditions and in the same apparatus as in the preceding work.

Zinc. Two series of experiments conducted at different times led to identical results: it was shown that the half wave potential did not depend on the concentration of the addendum. In spite of the fact that from 0.2 to 0.8 mole/liter of the latter was added and its concentration exceeded the concentration of zinc ions by 50-200 times, the magnitude of $E_{1/2}$ remained unchanged within the limits of experimental error (± 2 mV). Addition of thiourea to the simple zinc ion in a background of 0.1 N KCl displaced the potential to the opposite side by 10-14 mV, as if a chloride complex of zinc was decomposed, if one considers the action of the "background" as weak complex formation.

TABLE 1

Metal ion	Covalent index	$K_{instability}$
Hg^{2+} . .	228	10^{-28}
Cd^{2+} . .	159	$1.2 \cdot 10^{-3}$
Pb^{2+} . .	156	$1.7 \cdot 10^{-2}$
Zn^{2+} . .	136	Complex absent
Ni^{2+} . .	97	The same and displacement of $E_{1/2}$ to the opposite side

It is thus evident that zinc does not form a complex with thiourea in aqueous solution.

Nickel. While in the case of zinc the displacement under the same concentration of addendum is expressed in tenths of mV, in the case of nickel this displacement amounts to about 200 mV. It is well known from the literature data that such a phenomenon is repeatedly observed. For example, it follows from the data of Kolthoff and Lingane [4] that $E_{1/2}$ of the nickel ion in 1N KCNS is displaced by 400 mV to the opposite side in relation to $E_{1/2}$ of the same ion in 1N KCl. The same thing is observed in the reaction of the nickel ion with pyridine.

It follows from these data that the sequence of the series of metals is preserved, since the stability of these complexes in solution diminishes with decrease in the covalent indices (Table 1).

Bismuth. The complex compound of the trivalent bismuth ion with thiourea has long been utilized both to detect Bi^{3+} and for its quantitative determination.

In agreement with the literature data, in the solid form several different thiourea complexes of bismuth exist.

According to the communication of Babko and Pilipenko [5], the soluble complex with a coordination number of 9 and a dissociation constant of $6.4 \cdot 10^{-2}$ (this was apparently sequential) has the most intense coloration.

In the article of Yatsimirsky and Atasheva [6] there is an indication concerning the preparation of a complex with a coordination number of 6, which is found to be in agreement with the value found in the present work.

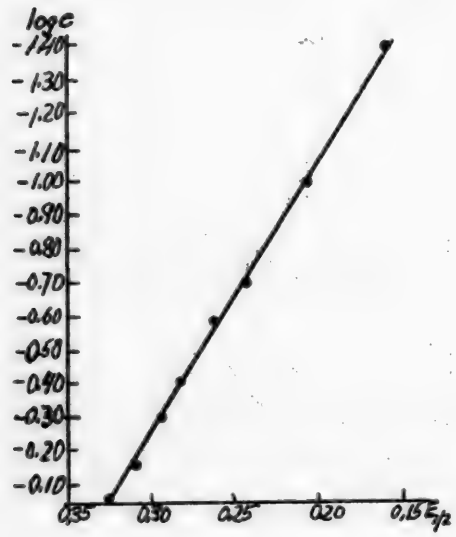

Fig. 1. Curve of the dependence of log c on $E_{1/2}$ for the determined composition of the thiourea complex.

The coexistence of several complexes of bismuth with thiourea is entirely possible under various conditions, and the goal of the present work was, consequently, not only to establish the composition of the complexes in aqueous solution, but also to determine the instability constant (general and sequential).

The conditions of the measurements differed from [1] only in the fact that: 1) to avoid hydrolysis, the electrolyte was acidified to pH 0.32; and 2) the bismuth concentration amounted to $2.7 \cdot 10^{-3}$ mole/liter.

The reversibility of the process of discharging the bismuth ion was established from the experimental data accumulated by us.

Actually, from consideration of the equation of the polarographic wave, the tangent of the angle of inclination (at n = 3) is seen to be equal to $\frac{0.059}{3} = 0.0197$, while the mean experimental value is equal to 0.021.

Determination of the composition of the thiourea complex, that is, the coordination number, was conducted by constructing a graph with the coordinates: $E_{1/2}$ – $\log c_{CSN_2H_4}$ (Fig. 1), from which it follows that the tangent of the angle of inclination $\frac{\Delta E_{1/2}}{\Delta \log c} = 0.117$, i.e., $p = 5.9 \approx 6$.

Evidently, in the range of change of concentration of the addendum of from 0.04 to 0.88 mole/liter, the composition of the complex cation is as follows: $[Bi(CSN_2H_4)_6]^{3+}$.

A shortened form of the well known formula was employed to calculate the instability constant:

$$\Delta E_{1/2} = -\frac{0.0591}{3} \log K_{instability} + p \frac{0.0591}{3} \log c_{CSN_2H_4} \qquad (1)$$

The ratio of the diffusion currents and the activity coefficient of the addendum was taken as unity.

In Table 2 the experimental data and the calculated magnitude of the instability constant are presented. Its mean value was equal to

$$1.09 \cdot 10^{-12} \pm 20\%.$$

Since equation (1) is represented by the straight line $y = a - bx$, then, using the method of least squares for calculation, it can be reduced to the form:

$$y = 0.2349 + 0.1157x, \qquad (2)$$

whence: $K_{instability} = 1.2 \cdot 10^{-12}$ and $p = 5.87$.

The results are in entirely satisfactory agreement.

TABLE 2

Experiment No.	$\Delta E_{1/2}$ (in V)	c in moles/liter of thiourea	$K_{inst.} \cdot 10^{-12}$
1	0.076	0.04	0.63
2	0.117	0.10	1.15
3	0.154	0.20	0.9
4	0.172	0.30	1.3
5	0.186	0.40	1.5
6	0.200	0.50	1.2
7	0.218	0.70	1.15
8	0.231	0.88	0.9
		Mean	1.09 ± 20%

The change in the thermodynamic potential in the ionization process can be enumerated from the magnitude of the ionization constant of the complex:

$$\Delta Z = -RT\ 2.3 \log K = 4 \cdot 575 \cdot$$

$$\cdot 298 \cdot 12 = 16360 \text{ cal.}$$

Since the composition and the stability of the bismuth complex can be determined only in acidic medium, it is evident that the acid, in the given case hydrochloric, playing the simultaneous role of background and addendum, will influence the magnitude of the instability constant.

The majority of the measurements were conducted at a pH of around 0.35. Variation of the magnitude of pH up to 6-7% had little influence, since the experimental error depended chiefly on the variation of the magnitude of $E_{1/2}$. During a more significant variation in pH the change in $K_{instability}$ became very noticeable, and with lowered pH the magnitude of the instability constant increased and vice versa. This is explained by the fact that the half wave potential of the complex ion responds less to change in pH than the half wave potential of the simple ion. It is evident from this that at low values of pH, $\Delta E_{1/2}$ is diminished while the instability constant is increased. I express thanks to K. B. Yatsimirsky for providing the subject and valuable counsel.

SUMMARY

1. The successive diminishing of stability with diminishing covalent index of a series of metal ions in combination with thiourea was confirmed.

2. The coordination number (p = 6) and the instability constant ($K_{instability} = 1.1 \cdot 10^{-12}$) of the thiourea complex of bismuth were determined.

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POLAROGRAPHIC INVESTIGATION OF THE HYDROGENATION PROCESS

III. HYDROGENATION OF ACETYLENEDICARBOXYLIC ACID

A. L. Markman

The question concerning the character of the process of saturation of compounds with a triple bond is associated with the problem of the selectivity of the hydrogenation process.

The majority of authors who have conducted the hydrogenation of acetylenic derivatives with a palladium catalyst, have noted the selective character of this process; a selective conversion of the acetylenic compound into an ethylenic proceeds initially, and only in the second instance does conversion of the ethylenic into the corresponding saturated derivative occur. The rate of hydrogenation in the second stage can be greater, equal to, or less than the rate of hydrogenation in the first stage, depending on the functional nature of the compound being hydrogenated.

Bourguel [1] described an experiment involving the catalytic hydrogenation of acetylenedicarboxylic acid in the presence of colloidal palladium and starch as a protective colloid; maleic acid was obtained. Ott and Schröder [2], in a study of the semisaturation products of acetylenedicarboxylic acid, found that during rapid hydrogenation, the sole reaction product was maleic acid, while during slow hydrogenation—fumaric acid was produced, which was apparently a secondary product of the conversion.

In contrast to palladium catalysts, platinum catalysts (platinum black, platinum hydrosols) according to the data of the majority of authors, cause unselective hydrogenation of acetylenic derivatives, characterized by the absence of a break in the rate of the process after half saturation of acetylene. We have not encountered in the literature attempts to hydrogenate acetylenedicarboxylic acid in the presence of platinum.

EXPERIMENTAL

We summarize the data of one experiment of the hydrogenation of acetylenedicarboxylic acid.

0.57 g of acetylenedicarboxylic acid; 105 mg of Al and 32 mg of Pd; and 40 ml of alcohol were taken. The bath temperature was 25°, the air temperature was 26°, the pressure 717 mm; the theoretical absorption of hydrogen H_0 = 260 ml.

τ*	1	2	3	4	5	6	7
V**	7.2	13.2	18.2	23.6	28.6	34.0	38.6
τ	8	9	10	11	12	13	14
V	43.8	48.6	53.0	58.6	63.4	68.4	72.6
τ	15	16	17	18	19	20	21
V	77.2	81.6	85.6	90.2	94.2	97.2	101.4
τ	22	23	24	25	26	27	28
V	105.2	108.8	112.0	115.4	118.4	121.8	124.8
τ	29	30	31	32	33	34	35
V	127.8	130.8	133.8	136.0	138.4	140.8	142.4
τ	36	37	38	39	40	41	
V	144.8	148.0	150.0	152.0	153.8	155.6	
τ	42	43	44	45	46	47	
V	157.6	159.0	160.6	162.0	163.6	165.2	
τ	48	49	50	51	52	53	
V	166.8	168.0	169.4	170.6	172.0	173.2	
τ	54	55	56	57	58	59	
V	174.4	175.8	177.0	178.0	179.0	180.0	
τ	60	61	62	63	64	65	
V	181.0	183.0	184.4	185.6	186.8	187.6	
τ	66	67	68	69	70	71	
V	188.6	189.6	190.6	191.6	192.6	193.4	etc.

*Time in minutes.

**Volume in milliliters.

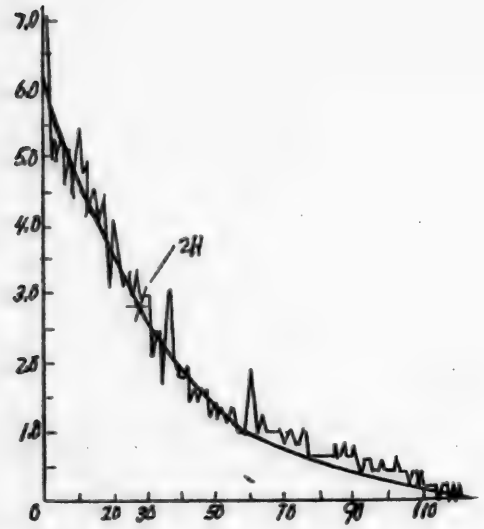

Fig. 1. Curve of the rate of absorption of hydrogen. Explanation in the text.

The curve of Figure 1 is plotted from the data of this experiment; the rate of absorption of hydrogen is plotted on the ordinate (ml/minute). No break in the curve is observed after the absorption of the first 2H: the rate of absorption of hydrogen falls from the first to the last minutes of the process; its fall, at the beginning more rapid, becomes retarded toward the end.

We employed the polarographic analysis method to study the process of catalytic hydrogenation of acetylenedicarboxylic acid as in the preceding work [3].

The methodology of the polarographic investigation of mixtures of acetylenedicarboxylic and maleic acids has been described earlier [4]. The presence of succinic acid as a third component in the mixture does not interfere with the determination of the quantities of the two unsaturated acids, since succinic acid does not give polarographic waves.

We used the single stage method of polarography for which mixtures were employed that were formed at various stages of the hydrogenation in aqueous solutions with a buffered background of 1 N HCl at pH 2.7 and $\underline{t}$ 25°, $\underline{v}$ = 14 drops/minute. Under these conditions the half wave potential of the total wave (maleic acid and the first wave of acetylenedicarboxylic acid) lies at −0.80 V, the second wave of acetylenedicarboxylic acid at −1.15 V. The coefficient of proportionality (between the diffusion current and the concentration) under the indicated conditions was equal for maleic acid, to:

$$\left(\frac{i'_d}{c}\right)_{av.} = 4.76 \cdot 10^3$$

and for the second wave of acetylenedicarboxylic acid,

$$\left(\frac{i''_d}{c}\right)_{av.} = 5.89 \cdot 10^3;$$

the ratio of the magnitudes of the diffusion currents for the first and second waves of acetylenedicarboxylic acid

$$\frac{i'_d}{i''_d} = 0.0407.$$

As a consequence of the small magnitude of this ratio at low contents of acetylenedicarboxylic acid in the mixtures one can, without great error, consider the wave lying at the more positive potential values as the wave of maleic acid.

In addition, the polarographic method was employed with added standard solution.

One series of polarograms obtained from a series of samples removed from the acetylenedicarboxylic acid solution during its hydrogenation is presented in Fig. 2. Curve 1 refers to the initial solution: only one wave is observed on it, that of acetylenedicarboxylic acid. Two waves are observed on Curves 2-6 −all are diminished in the height of the acetylenedicarboxylic acid wave and at a more positive potential all are increased in the total wave of maleic and acetylenedicarboxylic acids. Only one wave is still evident in Curves 7-9, that of maleic acid, the height of which also gradually falls in proportion to the conversion of maleic acid into succinic acid. Finally, in Curve 10, taken after cessation of hydrogen absorption, no waves are observed, since at this time only succinic acid is found in the solution.

Hydrogenations of acetylenedicarboxylic acid and also of mixtures of acetylenedicarboxylic and maleic acids in the presence of palladium and platinum were conducted.

Hydrogenation of Acetylenedicarboxylic Acid

1. Hydrogenation of Acetylenedicarboxylic Acid in the Presence of Palladium. 114 g of acetylenedicarboxylic acid; 210 mg of Al and 64 mg of Pd; 30 ml of alcohol and 10 ml of water were taken. The temperature of the bath was 25° and of air 22°, the pressure was 713.5 mm; the theoretical absorption H_0 = 515.6 ml. For the polarography 1.0 ml of each sample was diluted with buffer with a pH of 2.7 to a volume of 50 ml. The half-wave potential: total half waves −0.75 V, second wave of acetylenedicarboxylic acid −1.13 V (Table 1, Fig. 3).

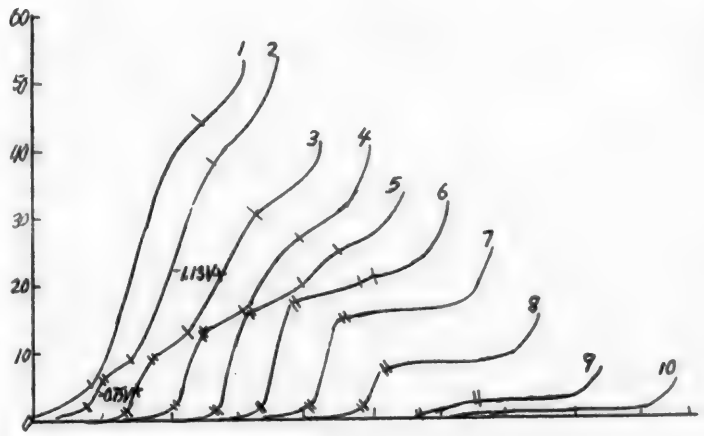

Fig. 2. Series of polarograms of samples of acetylenedicarboxylic acid in the course of hydrogenation. Explanation in the text.

Curve a on Fig. 3 represents the disappearance of acetylenedicarboxylic acid in proportion to the absorption of hydrogen expressed in percentages of the initial quantity; the curve m—the disappearance of maleic acid and the simultaneous accumulation of succinic acid, expressed in percentages of that quantity which would accumulate as a result of complete hydrogenation. Here, the saturation curve during a completely unselective process would coincide with the diagonal AC. During a strictly selective process acetylenedicarboxylic acid would be saturated along the broken line ADC, maleic acid along the broken line ABC. In the given case the degree of selectivity can be measured by the ratio of the area of the figure AaCmA to the area of the parallelogram ABCD. For this case it was found that p_1 = 0.1817, p_2 = 0.1721, S = 0.920.

This same curve characterizing the course of the saturation of acetylenedicarboxylic and maleic acids, can also serve as the curve of the change in composition of the tricomponent mixture (acetylenedicarboxylic-maleic-succinic acid) in the course of hydrogenation. Here 1—the field of existence of acetylenedicarboxylic acid, 3—the field of existence of succinic acid, 2—the field of existence of maleic acid.

TABLE 1

Amount of H_2 absorbed (in %)	Acid concentration · 10^5			Composition of the acid mixtures (in %)		
	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid
0	500	0	0	100.0	0	0
10.0	400	100	0	80.0	20.0	0
20.3	296	204	0	59.2	40.8	0
31.0	190	310	0	38.0	62.0	0
41.8	107	368	25	21.4	73.6	5.0
53.1	54	361	85	10.8	72.2	17.0
64.5	0	355	145	0	71.0	29.0
76.3	0	237	263	0	47.4	52.6
88.4	0	116	384	0	23.2	76.8
90.0	0	100	400	0	20.0	80.0

Evidently, during a completely unselective hydrogenation, when each molecule of maleic acid, immediately after its formation, would be converted into a molecule of succinic acid, we would not have a field of

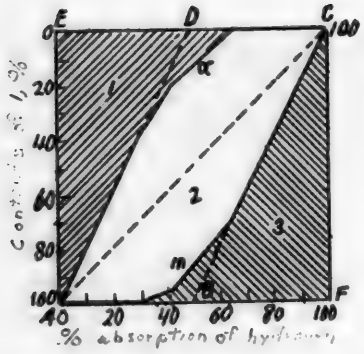

Fig. 3. Hydrogenation of acetylenedicarboxylic acid. Palladium as the catalyst. Explanation in the text.

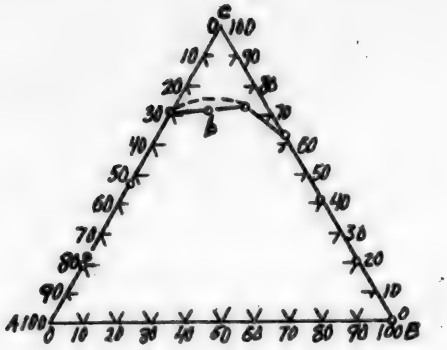

Fig. 4. Composition diagram of the tricomponent mixture of acids: A) succinic, B) acetylenedicarboxylic, C) maleic acid.

maleic acid; the diagonal AC would serve as the boundary between the acetylenedicarboxylic acid AEC and the succinic acid AFC. During strictly selective hydrogenation the field of existence of acetylenedicarboxylic acid would be the triangle AED, of maleic acid—the parallelogram ABCD, and of succinic acid—the triangle BFC. The less selective the hydrogenation, the narrower should be the field of existence of maleic acid AaCmA; however, it will always stretch along the diagonal AC, separating the field of acetylenedicarboxylic acid from the field of succinic acid.

A composition diagram of the tricomponent mixture is presented in a triangular system of coordinates in Fig. 4. The points on the curve of this figure show the composition of samples taken from the duck at various stages of the hydrogenation. The point b corresponds with the initial composition of the product being hydrogenated (100% acetylenedicarboxylic acid). If the process were proceeding strictly selectively, that is, if the acetylenedicarboxylic acid were initially converted into maleic acid and only later, after the disappearance of all the acetylenedicarboxylic acid were the maleic acid converted into succinic, then the change in the composition of the mixture would proceed along the broken line BCA. During a completely unselective hydrogenation or during a selective and preferential saturation of maleic acid, the molecules of this acid at the moment of their formation from half-saturated acetylenedicarboxylic acid would be instantly hydrogenated along with, or preferably before the acetylenedicarboxylic acid, with conversion into succinic acid. In such a case, at any moment of the process we would have a right to expect the presence in the mixture of only two acids—acetylenedicarboxylic and succinic; the change in composition would proceed along the straight line BA.

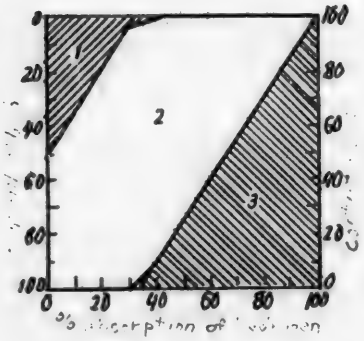

Fig. 5. Hydrogenation of acetylenedicarboxylic and maleic acids. The catalyst was palladium. Acids: 1) acetylenedicarboxylic; 2) maleic; 3) succinic.

The character of the process which has been established appears rather highly selective, which agrees with the literature data pertaining to the hydrogenation of acetylenic derivatives and, in particular, of acetylenedicarboxylic acid in the presence of palladium catalyst. Such a character of the process permits us to assume that the maleic acid formed after the half saturation of acetylenedicarboxylic acid is desorbed from the surface of the catalyst and passes into the body of the medium, yielding its place to new molecules of acetylenedicarboxylic acid.

It should be noted that in the first half of the process 5.76% of the initial quantity of acetylenedicarboxylic acid per minute disappears, on the average and 1.10% (of the final quantity) of succinic acid is formed; the first figure characterizes the rate of half saturation of acetylenedicarboxylic acid; the second the rate of saturation of maleic acid; the first quantity is almost 5 times greater than the second.

TABLE 2

Amount of H_2 absorbed (in %)	Acid concentration · 10^5			Composition of the acid mixtures (in %)		
	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid
0	250	250	0	50.0	50.0	0
10.1	174	326	0	34.8	65.2	0
20.4	97	403	0	19.4	80.6	0
30.9	18	482	0	3.6	96.4	0
41.7	0	438	62	0	87.4	12.6
52.7	0	354	146	0	70.8	29.2
64.1	0	270	230	0	54.0	46.0
75.8	0	182	318	0	36.4	63.6
79.5	0	154	346	0	30.8	69.2

TABLE 3

Amount of H_2 absorbed (in %)	Acid concentration · 10^5			Composition of the acid mixtures (in %)		
	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid
0	500	0	0	100	0	0
19.9	392	16	92	78.2	3.2	18.4
34.2	311	34	155	62.2	6.8	31.0
48.5	237	38	225	47.4	7.6	45.0
57.4	187	48	265	37.4	9.6	53.0
60.0	174	48	278	34.8	9.6	55.6

2. Hydrogenation of a Mixture of Acetylenedicarboxylic and Maleic Acids in the Presence of Palladium. 0.57 g of acetylenedicarboxylic and 0.58 g of maleic acid; 210 mg of Al and 64 mg of Pd; 30 ml of alcohol and 10 ml of water were taken. The temperature of the bath was 25°, of air 12°, the pressure 734.5 mm; the theoretical absorption H_0 = 363 ml (Table 2).

Although in a given case a significant quantity of maleic acid may be contained in a starting mixture with the same origin, nevertheless, as is evident from Fig. 5, the process proceeds selectively in the first stage at the expense of the preferential half saturation of acetylenedicarboxylic acid. For this experiment the following values were found: $p_1 = 0.2343$; $p_2 = 0.2332$; $S = 0.995$.

The saturation of an equimolar mixture of acetylenedicarboxylic and maleic acids in the presence of palladium is represented in a triangular system of coordinates in Fig. 6. For this the following values were found: $p_1 = 0.1567$; $p_2 = 0.1558$; $S = 0.995$; that is, the same values as for Fig. 5.

3. Hydrogenation of Acetylenedicarboxylic Acid in the Presence of Platinum. Experiment A. 1.14 g of acetylenedicarboxylic acid; 210 mg of Al and 116 mg of Pt; 30 ml of alcohol and 10 ml of water were taken. The temperature of the bath was 25°, of air 26°, the pressure was 715 mm; the theoretical absorption H_0 = 516 ml (Table 3).

The corresponding graph is presented in Fig. 7. $p_1 = 0.1845$; $p_2 = 0.0148$; $S = 0.080$ were found for it.

Since the saturation of acetylenedicarboxylic acid in the presence of platinum did not go to completion in a number of experiments, a hydrogenation experiment was set up at a somewhat higher temperature – at 40° and with a larger quantity of the platinum catalyst.

Experiment B. 1.14 g of acetylenedicarboxylic acid; 420 mg of Al and 232 mg of Pt; 20 ml of alcohol and 20 ml of water were taken. The temperature of the bath was 40° and of air was 15°, the pressure was 723 mm; the theoretical absorption H_0 = 496.8 ml. The conditions of the polarography were analogous to those of the preceding experiment (Table 4).

Fig. 6. Composition diagram of the tricomponent mixture of acids: A) succinic; B) acetylenedicarboxylic; C) maleic.

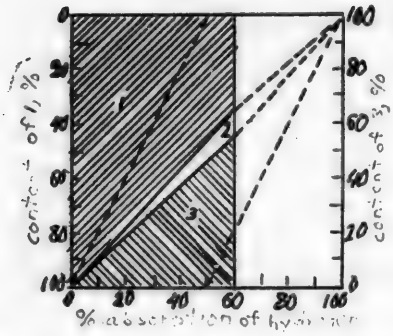

Fig. 7. Hydrogenation of acetylenedicarboxylic acid. Catalyst: platinum. Acids: 1) acetylenedicarboxylic; 2) maleic; 3) succinic.

TABLE 4

Amount of H_2 absorbed (in %)	Acid concentration · 10^5			Composition of the acid mixtures (in %)		
	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid
0	500	0	0	100	0	0
29.1	330	49	121	66.0	9.8	24.2
42.1	251	77	172	50.2	15.4	34.4
61.4	160	76	264	32.0	15.2	52.8
72.4	103	67	330	20.6	13.4	66.0
76.1	88	59	353	17.6	11.8	70.6

$p_1 = 0.1858$; $p_2 = 0.0354$; S = 0.190 were found for the corresponding Fig. 8.

It is noteworthy that the saturation of acetylenedicarboxylic acid (and also of its mixtures with maleic acid) does not go completely in the presence of platinum. It is impossible to explain this phenomenon by a poisoning action of some one of the three acidic components of the reaction mixture: in the first place, the hydrogenation of this very acetylenedicarboxylic acid proceeds completely in the presence of palladium, and, in the second place, the hydrogenation of maleic acid in the presence both of palladium and of platinum also proceeds completely without difficulties. The cause of the indicated phenomenon remains unexplained for us.

Figures 9 and 10 were plotted in a triangular system of coordinates from the data of the experiments of saturating acetylenedicarboxylic acid in the presence of a platinum catalyst. $p_1 = 0.1724$; $p_2 = 0.0138$; S = 0.080, were found for Experiment A; $p_1 = 0.1694$; $p_2 = 0.0329$; S = 0.190, were found for Experiment B, that is, exactly the same values for the index of selectivity S as we obtained from Fig. 7 and 8.

As is evident from Figs. 9 and 10, the saturation curves of acetylenedicarboxylic acid lie much closer to the straight line AB than to the broken line ACB. This indicates that the maleic acid formed as a

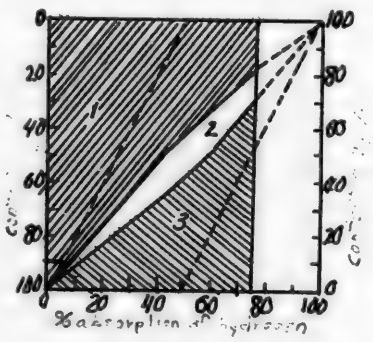

Fig. 8. Hydrogenation of acetylenedicarboxylic acid at 40°. Catalyst: platinum. Acids: 1) acetylenedicarboxylic; 2) maleic; 3) succinic.

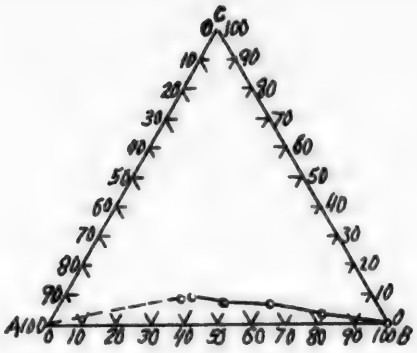

Fig. 9. Composition diagram of the tricomponent mixture of acids: A) succinic; B) acetylenedicarboxylic; C) maleic. Catalyst: platinum. At 25°.

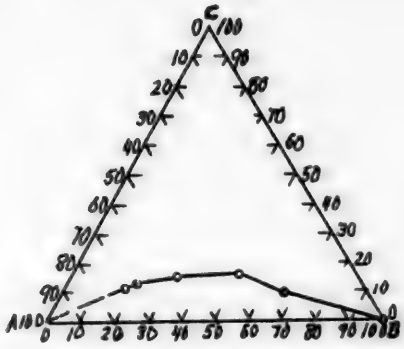

Fig. 10. Composition diagram of the tricomponent mixture of acids: A) succinic; B) acetylenedicarboxylic; C) maleic. Catalyst: platinum. At 40°.

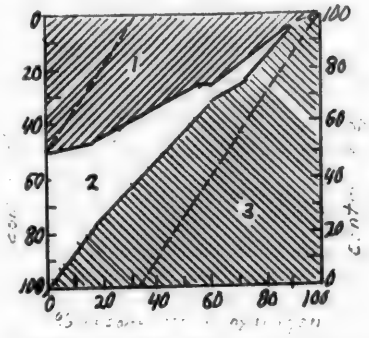

Fig. 11. Hydrogenation of a mixture of acetylenedicarboxylic and maleic acids. Catalyst: platinum. At 40°. Acids: 1) acetylenedicarboxylic; 2) maleic; 3) succinic.

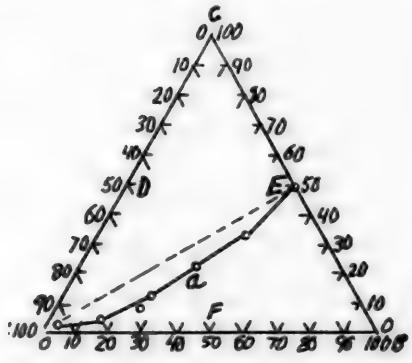

Fig. 12. Composition diagram of the tricomponent mixture of acids: A) succinic; B) acetylenedicarboxylic; C) maleic.

TABLE 5

Amount of H_2 absorbed (in %)	Acid concentration · 10^5			Composition of the acid mixtures (in %)		
	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid	Acetylene-dicarboxylic acid	Maleic acid	Succinic acid
0	250	250	0	50.0	50.0	0
17.6	227	162	111	45.4	32.4	22.22
37.6	176	110	214	35.2	22.0	42.8
54.2	132	62	306	26.4	12.4	61.2
60.5	129	36	335	25.8	7.2	67.0
75.0	72	21	407	14.4	4.2	81.4
90.9	15	10	475	3.0	2.0	95.0

result of the half saturation of acetylenedicarboxylic acid is for the most part instantly further saturated —to succinic acid. Evidently, one can assume that a molecule of acetylenedicarboxylic acid which is not desorbed from the surface of the catalyst after half saturation, then and there reacts with a second hydrogen molecule. On the

other hand, one can assume that after half saturation the molecule escapes into the medium and that subsequently, of the two acids found in the reaction media – acetylenedicarboxylic and maleic – maleic acid is preferentially absorbed and hydrogenated on the surface of the platinum.

The accumulation of maleic acid in the medium, although in very small quantities, in the course of the hydrogenation (Fig. 7 and 8) suggests that the second explanation is more correct. Hydrogenation of a mixture of acetylenedicarboxylic and maleic acids in the presence of a platinum catalyst conclusively resolved this question.

4. Hydrogenation of a Mixture of Acetylenedicarboxylic and Maleic Acids in the Presence of Platinum. 0.57 g of acetylenedicarboxylic and 0.58 g of maleic acids; 420 mg of Al and 232 mg of Pt; 20 ml of alcohol and 20 ml of water were taken. The temperature of the bath was 40°, of air 14°, the pressure was 726.5 mm; the theoretical absorption H_θ = 369 ml. The conditions of the polarography were the same as in the preceding experiments (Table 5).

The change in the composition of the mixture in the course of hydrogenation is depicted in Fig. 11, and in a triangular system of coordinates in Fig. 12.

Let us consider what character Fig. 12 would have during various possible directions of the process.

1. During selective half saturation of acetylenedicarboxylic acid, as it occurs in the presence of palladium, the process would proceed along the broken line E CA.

2. During selective saturation of acetylenedicarboxylic acid into succinic (without desorption of the maleic acid formed as an intermediate) the process would proceed along the broken line EDA.

3. During an absolutely unselective hydrogenation of both unsaturated acids with the conversion of both into succinic acid the process would proceed along the straight line EA. But this means that, in order that it should be hydrogenated to the same extent as the acetylenedicarboxylic acid, the maleic acid should not be linked by its origin with the half saturation of acetylenedicarboxylic acid, and therefore should not be bound by the surface of the catalyst; it can appear on the surface from the body of the medium.

4. During a selectively preferential saturation of maleic acid the process would proceed along the broken line DFA. But, in this case, the "volumetric origin" of maleic acid had been certainly accomplished already.

The saturation in fact proceeds along the curve EaA, lying between the straight line EA and the broken line EFA. Such a location for the saturation curve in the first place conclusively persuades one of the fact that maleic acid proceeds to the surface of the catalyst from the body of the medium and, in the second place, it leads to the similar conclusion that the palladium preferentially and with a high degree of selectivity hydrogenates acetylenedicarboxylic acid, converting it into maleic acid, and that platinum preferentially, although not so strictly selectively, converts maleic acid into succinic acid.

Turning once more to Fig. 12, it should be noted that during saturation along the broken line ECA the rate of saturation of maleic acid in the first half of the process would be equal to zero; during the process proceeding along EDA, the ratio of the saturation rates of maleic and acetylenedicarboxylic acids in the first stages of this process would be equal to 1:1, during the process along the straight line EA this ratio over its entire extent would be equal to 2:1, and finally, during the process along EFA the rate of saturation of acetylenedicarboxylic acid in the first half would be equal to zero. In fact, during the first half of the process 0.55% of acetylenedicarboxylic acid disappears per minute and 1.42% of succinic acid is formed at the expense of the saturation of maleic acid. Thus, the ratio of the rates of saturation of maleic and acetylenedicarboxylic acids turns out to be equal to 1.42:0.55 = 2.6:1, which causes the saturation curve to take a position between EA and EFA

SUMMARY

1. It was established that acetylenedicarboxylic acid is hydrogenated in the presence of palladium at a rate which gradually falls from the beginning to the end without a break in the curve after the absorption of the first two hydrogen atoms.

2. During the hydrogenation in the presence of palladium, acetylenedicarboxylic acid in the first stage is almost completely converted into maleic acid and only in the second stage is maleic acid hydrogenated into succinic acid; the process is of a strictly selective nature. In the presence of platinum the acetylenedicarboxylic acid is at once hydrogenated to succinic acid with, however, the simultaneous formation of small quantities of maleic acid. In mixtures of acetylenedicarboxylic and maleic acids in the work with palladium in the first stage, the half saturation of acetylenedicarboxylic acid proceeds almost strictly selectively; in the work with platinum in the first stage, maleic acid is saturated, although not strictly selectively. It was established that during the

hydrogenation of acetylenedicarboxylic acid in the presence of either catalyst, the maleic acid formed in the course of the process is desorbed and escapes into the body of the medium, whence it is subsequently once more adsorbed, possibly on other active centers.

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THE HYDROGEN BOND AND THE DENSITY OF SOLUTIONS

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In benzene solutions a dissolved substance that is capable of forming hydrogen bonds as a rule preserves its tendency toward association due to the hydrogen bonds between the molecules; in alcohol, however, as is supposed [1], association between the molecules of the same substance in the majority of cases diminishes the association with the solvent molecules. In either case the extent to which association of the molecules influences the density of the solutions is of interest.

To detect the influence of association one must first of all exclude or take account of the influence of other properties of the molecule, such as mass and size, on the density. This can be achieved according to a well-known method, by comparison of the density of the solutions samples of identical weight dissolved in identical volumes of solvent. In fact, the density of the solution $d = m_1n_1 + m_2n_2$, where m_1 and n_1 are the mass and number (per unit volume of the solution) of the molecules of the dissolved substance, m_2 and n_2 the mass and number of molecules of the solvent. In the solutions indicated above, m_1n_1 are identical for various substances. The greater the value of n_2, the less is n_1 and the molecular size of the dissolved substance and the greater the coupling forces of the molecules of the dissolved substance between each other and with the solvent molecules. Inasmuch as the molecular size in an enormous number of compounds varies parallelly with their masses, its influence on n_2 is to a considerable extent compensated for by the influence of n_1. As a result, the difference in n_2 and, hence, in the value of the density of such solutions, should, evidently, chiefly determine the differences in the coupling forces (including hydrogen bonds) of the molecules of the solute between themselves and with solvent molecules.

To answer the question raised above, the values of the density of solutions of the indicated type in benzene and alcohol at 50° of 42 compounds were determined and are summarized in Tables 1, 2, and 3. As follows from the data summarized in the tables, in the case of solutions of monosubstituted benzenes, the functional groups are arranged in series according to the value of the density of the solutions:

for solutions in benzene – $NO_2 > COOH > OH \approx COCH_3 > CHO > OCH_3 > CH_3$;

for solutions in alcohol –

$$COOH \approx NO_2 > OH > CHO > COCH_3 > COOC_2H_5 > OCH_3 > CH_3.$$

As was expected, the functional groups with the greater group moment and hence with greater coupling forces give solutions of higher density. These groups are arranged in the series on the basis of the group moments corresponding to them. Only phenol and particularly benzoic acid give solutions of appreciably higher density than follows from their group moment.

The density of a solution of phenol in benzene and alcohol is appreciably higher than that of the corresponding solutions of anisole. This was also observed in the case of the methyl ethers of the cresols and of the m- and p-isomers of various substituted phenols. At the same time the magnitude of the reduction in the density in the case of the ethers in comparison with the density of the initial hydroxy compounds was almost the same in all cases: in benzene it varied between 0.0025-0.0036, and in alcohol between 0.0022-0.0031. This same thing was observed in the case of solutions of acids, the ethyl esters of which yield solutions with a density 0.0040 (in alcohol) and 0.0036 (in benzene) less than the corresponding acids.

Solutions of metameric compounds not containing the hydroxyl group (for example, anisole and the m- and p-methoxybenzaldehydes), possess both in benzene and in alcohol a lower density than solutions of the corresponding

TABLE 1

Density of Solutions in Benzene at 50° ± 0.1° (Weighed Portions of 0.9984-0.9990 g in ~25 ml of Solution

Compound		d_4^{50}	Difference in the density of the solution		
			$d_m - d_o$	$d_p - d_o$	$d_{OCH_3} - d_{OH}$
Nitrobenzene		0.8593	–	–	–
Nitrophenol:	o-	0.8603	–	–	–
	m-	0.8636	+0.0033	–	–
	p-	0.8639	–	+0.0036	–
Nitroanisole:	o-	0.8609	–	–	+0.0006
	m-	0.8603	−0.0006	–	−0.0033
	p-	0.8603	–	−0.0006	−0.0036
Benzaldehyde		0.8552	–	–	–
Acetophenone		0.8557	–	–	–
Hydroxyacetophenone:	o-	0.8570	–	–	–
	m-	0.8588	+0.0018	–	–
	p-	0.8591	–	+0.0021	–
Methoxyacetophenone:	o-	0.8560	–	–	−0.0010
	m-	0.8560	0.0000	–	−0.0028
	p-	0.8563	–	+0.0003	−0.0028
Toluene		0.8462	–	–	–
Cresol:	o-	0.8537	–	–	–
	m-	0.8532	−0.0005	–	–
	p-	0.8536	–	−0.0001	–
Cresylmethyl ether:	o-	0.8511	–	–	−0.0026
	m-	0.8507	−0.0004	–	−0.0025
	p-	0.8509	–	−0.0002	−0.0027
Phenol		0.8556	–	–	–
Anisole		0.8528	–	–	−0.0028

TABLE 2

Density of solutions of substituted benzoic acids and derivatives of benzoic acid in benzene and alcohol at 50° ± 0.1° (weighed portions of 0.9990-0.9994 and 0.5000 g in 25 ml of solution).

Compound		d_4^{50} (in benzene)	d_4^{50} (in alcohol)	Difference in density of the solutions in alcohol	
				$d_p - d_o$	$d_{OR} - d_{OH}$
Benzoic acid		0.8574	0.7918	–	–
Ethyl benzoate		0.8538	0.7875	–	−0.0043
Hydroxybenzoic acid:	o-	–	0.7939	–	−0.0039
	m-	–	0.7956	–	−0.0042
	p-	–	0.7960	+0.0021	−0.0039
Methoxybenzoic acid:	o-	0.8528	0.7934	–	−0.0005
	p-	–	0.7936	–	−0.0024
Ethyl hydroxybenzoate:	o-	0.8509	0.7900	–	–
	m-	0.8514	0.7914	–	–
	p-	0.8519	0.7921	+0.0021	–
Ethyl methoxybenzoate:	o-	0.8510	0.7892	–	−0.0008
	p-	0.8514	0.7899	+0.0007	−0.0022

metamers containing the hydroxyl group (cresols, m- and p-hydroxyacetophenones).

That the indicated peculiarities were expressly evoked by a tendency toward the formation of hydrogen bonds between the molecules is indicated by the behavior of compounds studied with an intramolecular hydrogen bond such as the o-hydroxy-substituted nitrobenzene, benzaldehyde, acetophenone, benzoic acid and its ethyl ester. All these compounds preserve their tendency toward the formation of hydrogen bonds within the molecules in benzene

TABLE 3

Density of Solutions in Ethyl Alcohol at 50° ± 0.1° (Weighed Portion of 0.9980-0.9992 g in ~25 ml of Solution

Compound		d_4^{50}	Difference in the density of the solution		
			$d_m - d_o$	$d_p - d_o$	$d_{OCH_3} - d_{OH}$
Nitrobenzene		0.7918	–	–	–
Nitrophenol:	o-	0.7948	–	–	–
	m-	0.7958	+0.0010	–	–
	p-	0.7959	–	+0.0011	–
Nitroanisole:	o-	0.7937	–	–	−0.0011
	m-	0.7935	−0.0002	–	−0.0023
	p-	0.7933	–	−0.0004	−0.0026
Benzaldehyde		0.7887	–	–	–
Hydroxybenzaldehyde:	o-	0.7910	–	–	–
	m-	0.7938	+0.0028	–	–
Methoxybenzaldehyde:	o-	0.7915	–	–	+0.0005
	m-	0.7908	−0.0007	–	−0.0030
	p-	0.7910	–	−0.0005	–
Acetophenone		0.7880	–	–	–
Hydroxyacetophenone:	o-	0.7898	–	–	–
	m-	0.7919	+0.0021	–	–
	p-	0.7925	–	+0.0027	–
Methoxyacetophenone:	o-	0.7892	–	–	−0.0006
	m-	0.7895	+0.0003	–	−0.0024
	p-	0.7895	–	+0.0003	−0.0030
Toluene		0.7813	–	–	–
Cresol:	o-	0.7890	–	–	–
	m-	0.7884	−0.0006	–	–
	p-	0.7887	–	−0.0003	–
Cresylmethyl ether:	o-	0.7859	–	–	−0.0031
	m-	0.7862	+0.0003	–	−0.0022
	p-	0.7857	–	−0.0002	−0.0030
Phenol		0.7896	–	–	–
Anisole		0.7865	–	–	−0.0031

and, to a considerable extent, lack of capacity of forming complex molecules at the expense of the hydrogen bonds between them. As a result solutions of this sort of compound, in spite of the presence of the hydroxyl group, conduct themselves in a normal fashion. The density of the solutions of their methyl ethers, as a rule, differs in value from the density of the initial hydroxy compound only in the fourth place (in either direction). The density of a solution of o-methoxybenzaldehyde in alcohol, in contrast to what was observed in the case of the m- and p-isomers, is higher than the density of a solution of the metameric o-hydroxyacetophenone.

The absence of intermolecular association in the o-hydroxy compounds and its presence in their m- and p-isomers is explained by the unusual difference in the values of the density which is observed for solutions of isomers of the compounds under consideration. While the densities of the solutions of all three isomers of the unassociated methyl ethers or the cresols associated to an equal extent, differ from each other in either direction in the fourth place, in the case of the hydroxy compounds set forth above the density of a solution of the same concentration of the o-isomer is always less than that for their m- and p-isomers by 0.0018-0.0036 in benzene and 0.0010-0.0028 in alcohol.

Thus, both in benzene and in alcohol, in spite of the assumed difference in the character of the association, the formation of complexes between the molecules exhibits an identical influence on the density of the solutions not only qualitatively, but also for the most part quantitatively. This can be explained by the fact that in alcohol in the comparatively concentrated solutions studied by us complexes participate in the association with the solvent molecules, but not solitary molecules of this substance. In other words, complexes of the dissolved substance are evidently not completely destroyed in alcohol under the considered conditions. Complete destruction of intramolecular hydrogen bonds is also absent in alcohol.

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All the above established relationships for the density of solutions of various compounds in benzene and alcohol (and, according to certain data [2], they are also observed in such a solvent as amyl acetate) are similar to those which are observed for the individual substances in the liquid state. This permits us to determine the presence and character of association of the dissolved substance according to the density of the solutions of the corresponding compounds. The study of association of dissolved substance by the density of its solutions is particularly suitable for those organic compounds which readily undergo decomposition during fusion and in the liquid state, for example, for carboxylic acids of the aromatic series. Thus, the data summarized above for the density of solutions of hydroxy- and methoxybenzoic acids (Table 2) permit us to assume that in alcohol (and not only in benzene) salicylic acid conducts itself simultaneously as a compound with intramolecular hydrogen bonding and as an intermolecularly associated compound of the benzoic acid type; and that p-hydroxybenzoic acid is associated intermolecularly in two ways in alcohol: on the model of benzoic acid through the carboxyl group and on the model of the phenols through the hydroxyl group.

EXPERIMENTAL

The substances studied were synthesized and purified by methods described in the literature. The solvents were purified in the following way: pure benzene was treated with concentrated sulfuric acid, washed with solutions of alkali and water and then dried over calcium chloride; the dried benzene was redistilled in a column (1.5 meter), dried over metallic sodium and again redistilled in a column with a height of 1 meter. The alcohol was prepared by fractionally distilling rectificate in a column, steeping it over unslaked lime, with subsequent twofold redistillation..

The density was measured in a 25 ml pycnometer. The pycnometer was calibrated with benzene. The density of pure solvent d_4^{50} was taken for benzene to be equal to 0.8464, and for alcohol to be equal to 0.7778. The temperature of 50° was chosen because of the low solubility of the p-hydroxy isomers in benzene. A glass vessel about 20 liters in capacity served as thermostat.

The density values presented in the tables are the averages of several determinations which did not differ from each other by more than 3 units in the fourth place.

SUMMARY

1. The densities at 50° of solutions of 38 compounds in benzene and 42 compounds in ethyl alcohol were determined.

2. It was established that the same relationship of the densities of unassociated and associated inter- and intramolecular compounds as is observed for the individual substances in the liquid state is maintained in benzene and alcohol.

3. The data for the density of solutions can be utilized for the qualitative determination of the presence and character of the association of a dissolved substance.

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PHYSICO-CHEMICAL ANALYSIS OF THE NITRIC ACID – ACETIC ACID SYSTEM

ATOMIC CONCENTRATION AND CORROSIVE PROPERTIES OF THE SYSTEM

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A systematic study of the nitric acid – acetic acid system was conducted for the first time by Pictet [1], who proved that during the mixing of 2 moles of CH_3COOH with 1 mole of HNO_3 at 127-128°C a compound of the composition $HNO_3 \cdot 2CH_3COOH$ distils without decomposition, and who, among other things, showed the practical interest attaching to the giving system as a means for obtaining other nitration products in addition to those obtained by the usual nitration mixture. In recent years, the study of the given system has also been of interest from the point of view of the new theory of acids and bases of Hantzsch, Bronsted and Usanovich [2].

In 1940 Usanovich and Abidov [3], in a study of the nitric acid – acetic acid system as a nitration mixture, brought out a number of its peculiarities relative to the ordinary nitrating mixture (nitration of side chains and others). In recent years there has appeared a number of works of Miskidzhyan and Trifonov with their co-workers [4], who studied seven physico-chemical properties of the given system (fusibility, viscosity, density, refraction, surface tension, electrical conductivity and heat of solution). As a result of the study of the diagrams of fusion and viscosity, the system was shown to contain a chemical compound of the composition $HNO_3 \cdot CH_3COOH$. The study of the density was of a subsidiary character – the density was measured to estimate the internal friction, and these measurements were insufficiently precise. The study of the surface tension isotherm, the refractive index and the electrical conductivity of the system also did not enable the authors to confirm the presence of the chemical compound of Pictet; on the contrary, all the methods of investigation employed by the authors led to the conclusion that there was present in the solution a chemical compound of another composition, to wit: $HNO_3 \cdot CH_3COOH$.

Zaslavsky [5] in a number of his works, theoretically and experimentally demonstrated the possibility of utilizing the method of atomic concentrations for the physico-chemical study of systems of variable composition. If, during mechanical mixing of two bodies, the magnitude of the atomic concentration appears to be a linear function of the composition (in percentages by volume), then the chemistry taking place during the reaction of the substances always coincides to a greater or lesser degree with the deviations from additivity of the volumetric concentrations. The usual maximum ΔA corresponds to that composition of the new chemical compound which is formed as a result of the reaction of the mixed components, independently of the fact that this compound may also be found in a state of partial dissociation in the initial components.

Borodachev, in an experimental study of the atomic concentrations of the system under consideration, also enumerated the value of ΔA according to the data of Miskidzhyan and Trifonov, and showed that they had determined the specific gravity with insufficient precision. Consequently, to calculate the corresponding values of the atomic concentration, we undertook a special determination of the specific gravities of the mixtures. The corrosive properties of the system were simultaneously studied.

The preparation of chemically pure nitric acid was conducted according to Mishchenko's method [6]. The acid which was collected in the receiving flask had a very faint light lemon-yellow color; d_4^{25} 1.5064.

The acetic acid was prepared by twofold fractional crystallization of glacial acetic acid and subsequent threefold redistillation at 117° (754 mm); d_4^{25} 1.0493.

Atomic Concentration

The specific gravities of the mixtures were determined with a pycometer with a ground glass stopper and a capillary in a thermostat at 25°.

The observed specific gravities and the calculated values of the atomic concentrations of the mixtures are set forth in the table, where $d_{exp.}^{25}$ is the experimental specific gravity of the system and $d_{av.}$ is the calculated average value, $\Delta d = d_{exp.} - d_{av.}$, A and $A_{av.}$ are the experimental and calculated average atomic concentrations of the mixture, $\Delta A = A - A_{av.}$.

The small magnitude of the maximum values of ΔA is evidence of the insignificant chemical reaction between HNO_3 and CH_3COOH and the small stability of the compound obtained.

TABLE

Density of the system HNO_3—CH_3COOH and corrosion of steel in this system

Volumes %								Loss in weight of sample (in g)	Loss in weight of sample (in g/m² per 24 hrs)
HNO_3	CH_3COOH	$d^{25}_{exp.}$	$d_{av.}$	Δd	A	$A_{av.}$	ΔA		
0	100	1.0482	—	—	139.64	139.64	0	0.0663	207.2
10	90	1.1059	1.0939	0.0120	139.13	137.62	1.51	0.0120	37.5
20	80	1.1579	1.1396	0.0183	137.77	135.60	2.17	0.0017	5.3
30	70	1.2068	1.1853	0.0215	136.00	133.58	2.42	0.0007	2.3
40	60	1.2538	1.2310	0.0228	133.99	131.56	2.43	0.0007	2.1
50	50	1.3015	1.2767	0.0248	132.05	129.54	2.41	0.0007	2.2
60	40	1.3427	1.3224	0.0203	129.47	127.51	1.96	0.0013	4.0
70	30	1.3858	1.3682	0.0176	127.11	125.49	1.62	0.0019	5.9
80	20	1.4270	1.4139	0.0131	124.62	123.47	1.15	0.0023	7.2
90	10	1.4652	1.4596	0.0056	122.00	121.45	0.55	0.0034	10.6
100	0	1.5053	—	—	119.43	119.43	0	0.0050	15.6

The maximum ΔA corresponds to a compound of the composition $HNO_3 \cdot CH_3COOH$. This maximum was diffuse; evidently the mutual reaction of the components of the system does not go to conclusion and the following equilibrium is established between the components of the system and the compound being formed:

$$HNO_3 \cdot CH_3COOH \rightleftharpoons HNO_3 + CH_3COOH.$$

Our data, obtained by the method of atomic concentrations, are in agreement with the conclusions of Miskidzhyan and Trifonov.

Corrosive Properties of the System

After determination of the specific gravities of the prepared mixtures, they were used for the study of corrosive properties. About 50 ml of the mixture was poured into containers having capillaries in the lid. The containers were kept in a water thermostat for 2 hours at 25°. At the expiration of the indicated period a preliminarily prepared and weighed sample in the form of plates of dimensions 10 x 10 x 3 mm was dropped into the mixture.

The material of the plates was steel "2", containing 0.1% C, 0.41% Mn, 0.18% Si, 0.03% S, 0.033% P.

After 24 hours the steel samples were taken from the mixture, carefully and quickly washed with a large quantity of distilled water, with alcohol and ether and dried, after which they were weighed. We judged the corrosive action of the mixture by the loss in weight of the sample per 1 square meter of surface.

The results of our investigations are summarized in the last column of the table.

The corrosion of steel in mixtures of nitric and acetic acids is variable. The maximum loss in sample weight occurs in chemically pure CH_3COOH. In the subsequent mixtures with increase in HNO_3 content, the corrosion of steel is diminished, reaching a minimum at a HNO_3 content in the mixture of 40-50% (by volume); during further increase in HNO_3 content in the mixture the corrosion of the steel again gradually begins to increase and in chemically pure acid the loss in weight reaches a quantity of 15.6 g/m^2 per 24 hours.

Thus we see that the minimumloss in weight of the steel sample occurs in a mixture the composition of which corresponds to the compound $HNO_3 \cdot CH_3COOH$. The study of the corrosion properties of the system HNO_3—CH_3COOH furnishes yet another demonstration of the existence of the chemical compound $HNO_3 \cdot CH_3COOH$ in the system.

SUMMARY

1. The specific gravities of mixtures in the nitric acid — acetic system were determined at 25°.

2. The corrosive properties of the mixtures were studied [the losses in weight of steel samples (in grams) per square meter of surface per 24 hours were determined].

3. The presence in the system of a slightly stable compound $HNO_3 \cdot CH_3COOH$ was established by the data concerning the changes in deviations of the atomic concentrations (ΔA) from the calculated averages and the corrosive properties of the mixtures.

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INVESTIGATION OF THE SYSTEM: TETRANITROMETHANE – BENZENE BY VARIOUS PHYSICO-CHEMICAL ANALYTICAL METHODS

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Attention has frequently been directed to the fact that for the correct interpretation of the results of physico-chemical analysis, it is necessary to subject the system under investigation to thorough study and to make use of diverse methods. Complex investigation of systems by various methods of physico-chemical analysis is necessary to elucidate the possibilities of each of these methods and the conditions for their most effective and efficient applications.

However, materials for the comparison of the results of various methods of physico-chemical analysis have as yet been collected to an insufficient extent, and, in particular, there is little in the way of data for the comparative evaluation of the rapidly developing spectrophotometric method. The experimental material available concerning the absorption of light in solutions is very poor as regards complete data for binary liquid systems over the entire concentration range.

At the same time, for the comparison of spectrophotometry with other methods of physico-chemical analysis, it is particularly desirable to accumulate complete data specifically concerning binary systems.

We primarily selected the classical methods of the melting point diagram and the viscosity diagram for this comparison. In addition, as a special problem, we set up the comparison of spectrophotometric and refractometric data. The general nature of the physical causes evoking the phenomena of the absorption and refraction of light renders such a comparison very interesting and necessary for the determination of the role of the various factors influencing the form of the isotherm of the index of refraction.

We adopted the system: tetranitromethane – benzene as the subject of investigation; a system suitable for the study of various properties over the entire concentration range, and remarkable for the phenomenon of an intense yellow coloration obtained by mixing the colorless components. A similar coloration appears when tetranitromethane is mixed with many anionic organic compounds. The colorimetric study of this phenomenon has been the subject of several works [1, 2], which, as a rule, were conducted in ternary systems (in the presence of solvent) and apart from the investigation of other physico-chemical properties.

Only data concerning the density and surface tension at 25° [3] of the binary system under consideration are available in the literature; they were obtained in connection with the problem of calculating the parachor of methane derivatives, and were not interpreted with the object (of interest to us) of comparing the various physico-chemical analytical methods.

EXPERIMENTAL

Tetranitromethane was synthesized by the action of nitric acid on acetic anhydride [4, 5]. The product obtained by this method melted at 10-12°; neither by the steam distillation recommended for its purification nor by repeated fractional crystallization did we succeed in raising the melting point above 12.2°. A very effective method of purifying the tetranitromethane was treatment with concentrated sulfuric acid (half volume during energetic agitation for several minutes) with subsequent washing with water, drying, and a single crystallization. The product purified by this method had a m.p. of 13.9°, that is, much higher than that achieved via the more complicated repeated redistillation in a vacuum over phosphoric anhydride [6]. Comparison of the constants of our preparation with the best literature data (see Table 1) makes evident its higher degree of purity.

The benzene was the same as that used by one of us during the investigation of the dispersion of hydrocarbon mixtures [7].

The solutions were prepared in a quantity of 20-30 g in a small flask with a ground stopper; a sample weighed to an accuracy of 1 mg of the less volatile tetranitromethane was taken first. As a rule, immediately after preparing the mixtures, the viscosity, refractive indices and density were determined, after which the spectrophotometric and cryoscopic measurements were made in the same day.

TABLE 1

Constants of tetranitromethane

Properties	Preparation employed in present work	Literature data
Melting point	13.9°	13.8 [6]; 13.5 [3]
Density: d_4^{20}	1.6394	1.637* [8]; 1.638 [3]
d_4^{25}	1.6306	1.630 [6]; 1.629 [3]
Refractive index		
nD^{20}	1.4384	1.4384 [6]
nD^{25}	1.4360	1.4358 [6]
nC^{20}	1.4350	1.4349 [8]*
nC^{25}	1.4327	—
Mean dispersion		
ΔFC^{20}	120.8	120.5* [8]
ΔFC^{25}	120.4	—

The density was determined in a Biron pycnometer in a volume of about 12.5 ml. The d_4^{20} values in Table 3 refer to a vacuum and are precise to $1 \cdot 10^{-4}$ g/ml.

The viscosity was measured with an Ostwald viscosimeter of the usual type (diameter of the capillary ~0.4 mm) calibrated with benzene, the viscosity of which was taken as equal to 0.648 centipoise [9].

The refractive indices were measured for the sodium D line and the two C and F hydrogen lines on a Pulfrich refractometer (the latest prewar Zeiss model).

The measurements indicated were conducted in a thermostat with a temperature variation of not more than ± 0.02-0.03°.

The melting point was determined with an ordinary mercury thermometer with an accuracy of 0.1° by the cooling curve method.

The spectrophotometric measurements were conducted on a Beckmann model quartz spectrophotometer.

Closed cuvettes with quartz aperture of length 1 and 0.5 cm were used. (All the magnitudes for the optical densities on the figures are converted to a length of 1 cm.) A hydrogen lamp was the light source. The aperture width in all measurements was identical. The control cuvettes were filled with water. The average accuracy of the measurements was to 1% of the transmission.**

Results of the Investigation and Discussion of Them

The melting point diagram of the system under study (Fig. 1) is characterized by the presence of a simple eutetic and, consequently, does not yield any evidence of compound formation.

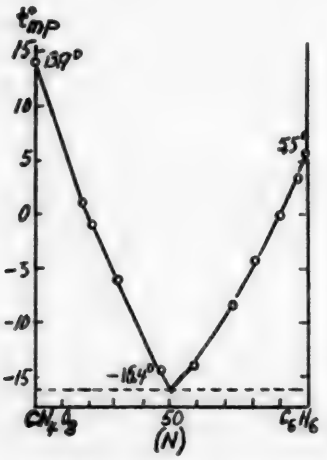

Fig. 1. Melting point diagram of the system: tetranitromethane — benzene.

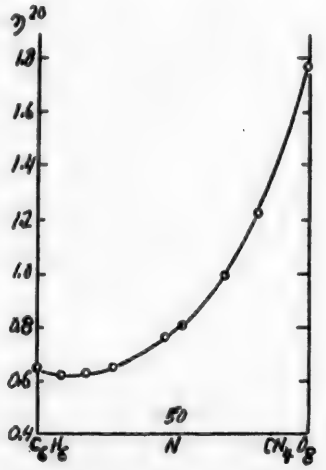

Fig. 2. Viscosity isotherm of the system: tetranitromethane — benzene at 20°

The viscosimetric data (Table 2) are found to be in agreement with the results of the thermal analysis. As is evident from Fig. 2, the viscosity isotherm η^{20} has a minimum which, although not very profound, is clear and is found outside the limits of possible experimental error. Such a form of the viscosity isotherm is encountered in systems with dissociation of an associated component. Viscosity minima are not observed in irrational systems of organic substances [10]. N. A. Trifonov [11, 12], in classifying the isotherms of viscosity and surface tension of binary

* Calculated from the data for 16.9° using the temperature coefficients found by us.

** M. E. Mogilev participated in the spectrophotometric measurements.

TABLE 2

Viscosity of the system: tetranitromethane – benzene at 20°

Content of benzene in mol. % (N)	Viscosity η^{20} (centipoises)
0	1.770
18.58	1.225
30.28	0.997
46.33	0.808
52.59	0.759
71.48	0.648
81.60	0.630
90.93	0.626
100	(0.648)

systems, does not exclude the possibility of the existence of minima in irrational systems, taking into account the formal possibility of any ratio between the magnitudes of the properties of the components and of the compound. These formal considerations, however, are certainly insufficient to cause one, solely on the basis of the form of the viscosity isotherm, to doubt that the system: tetranitromethane – benzene is irrational.

There is also a minimum on the surface tension isotherm, as is evident on Figure 3, plotted from the literature data [3]. The comments on the form of the viscosity isotherm set forth above are entirely applicable to the surface tension isotherm of the system being studied.

During the mixing of tetranitromethane with benzene a rather significant increase in volume (Table 3) is observed – a phenomenon which is usual in mixtures of chemically non-reacting substances. The deviations of the molar volume from additivity in the given system do not obey Biron's equation $\Delta My = KN_1N_2$ [13]: the coefficient K is not constant and depends on the concentration, as shown in Fig. 4. Recently, however, it has been noted [14], that Biron's equation is not observed in certain normal systems with markedly different molecular weights of the components, which is exactly what takes place in the given case. The expansion in the system under study is compared with the expansion in mixtures of benzene with saturated hydrocarbons in Fig. 5. It is easy to see that neither in the magnitude of the change in volume observed, nor in its dependence on the concentration of the system $C(NO_2)_4$–C_6H_6 does it in principle differ from mixtures of hydrocarbons.

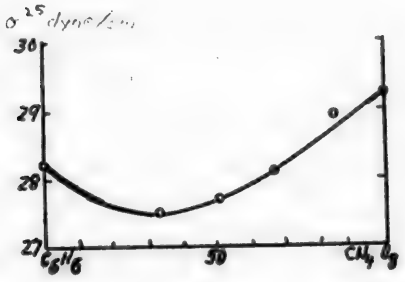

Fig. 3. Surface tension of mixtures of tetranitromethane with benzene (after data of Hammick and Wilmut [3]).

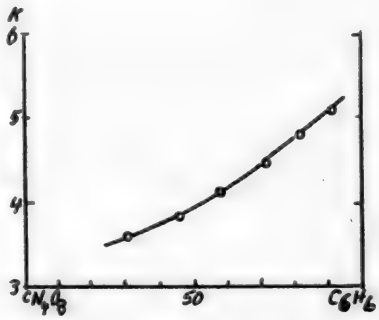

Fig. 4. Dependence of Biron's coefficient (K) on the concentration in the system: tetranitromethane – benzene.

TABLE 3

Density, refractive index and dispersion of the system: tetranitromethane – benzene

Content of benzene (in percentages								Deviations from additivity				
Gravimetric P	Volumetric V	Molar N	d_4^{20}	n_D^{20}	n_C^{20}	Δ_{FC}^{20}	ω_{FCD}^{20}	$\Delta v(P) \cdot 10^4$	$\Delta n_D(V) \cdot 10^4$	$\Delta n_C(V) \cdot 10^4$	$\Delta n_F(V) \cdot 10^4$	$\Delta\Delta_{FC}^{20}$
0	0	0	1.6394	1.4384	1.4350	120.8	27.55	–	–	–	–	–
14.75	24.40	30.28	1.4439	1.4505	1.4467	141.9	31.50	+ 47	–32	–33	–23	+ 9.9
25.59	39.09	46.33	1.3300	1.4586	1.4545	150.6	32.84	+ 68	–43	–45	–33	+ 11.9
35.65	50.83	58.17	1.2406	1.4658	1.4616	156.7	33.63	+ 79	–45	–47	–34	+ 12.6
50.41	65.48	71.84	1.1309	1.4755	1.4711	162.9	34.26	+ 81	–40	–42	–30	+ 12.1
63.87	76.73	81.60	1.0479	1.4831	1.4786	165.7	34.30	+ 72	–34	–36	–26	+ 9.8
79.97	88.16	90.93	0.9645	1.4916	1.4870	167.1	33.99	+ 46	–21	–22	–16	+ 5.9
100	100	100	0.8788	1.5011	1.4965	166.6	33.25	–	–	–	–	–

The refractive index isotherms n_D^{20}, n_C^{20} and n_F^{20} are convex toward the axis of composition (in volumetric portions). The deviations from additivity $\Delta\underline{n}(V)$ reach −0.0047, regularly decreasing from the red line C to the blue F line (Fig. 6). The negative values $\Delta\underline{n}(V)$ are customary for normal or associated components, but they are not encountered in typical irrational systems [16].

It is of interest that the isotherms of refractive dispersion have another direction of curvature than $\underline{n}(V)$. The average dispersion $\Delta_{FC}^{20} = (n_F^{20} - n_C^{20}) \cdot 10^4$ displays a considerable positive deviation from additivity ($\Delta\Delta_{FC}^{20}$) as a function of the volumetric proportions. The values $\Delta\Delta_{FC}^{20}$ reach + 12.6 (Fig. 6). Such a great positive deviation of the average dispersion from additivity in solutions is a rather rare phenomenon.

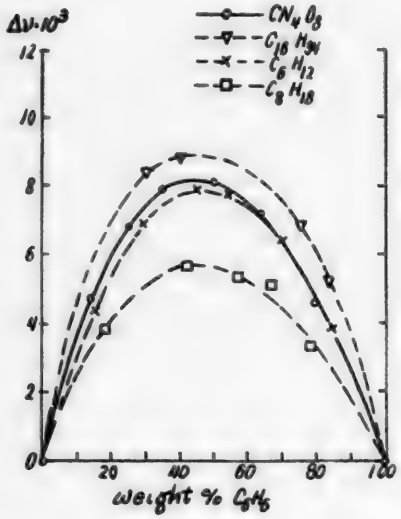

Fig. 5. Expansion in mixtures of benzene with tetranitromethane, cyclohexane [15], isooctane [14] and hexadecane [14].

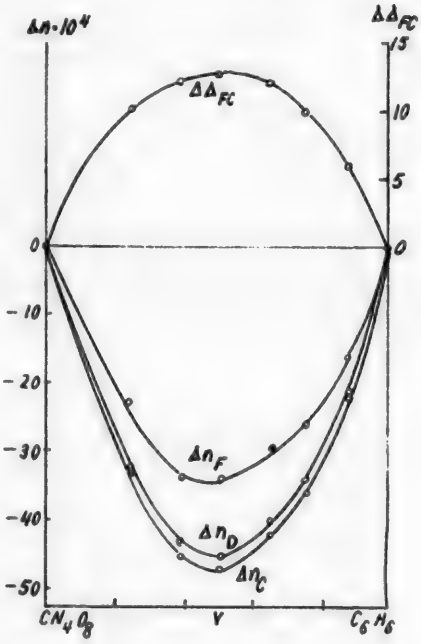

Fig. 6. Deviations from additivity of the indices of refraction and average dispersion.

The dispersive power $\omega_{FCD} = \dfrac{n_F - n_C}{n_D - 1} \cdot 10^3$ in the given system passes through a distinct maximum (Table 3). This, so far as is known, is the first case of a maximum ω_{FCD} in liquid systems.

The indicated peculiarities of refractive dispersion are doubtless associated with sharp changes in the absorption spectra in mixtures of tetranitromethane and benzene.

The results of the spectrophotometric investigations are presented in Fig. 7. On the curves of optical density − composition in the wave length range (422-458 mμ) studied, there are pronounced maxima at contents of benzene of 72-77 mol. %. Since tetranitromethane and benzene practically do not absorb in this region of the spectrum, the absorption which is observed in the mixtures must occur as the result of reaction of the components. There are no definite indications in the literature concerning the origin of the absorption band in mixtures of tetranitromethane with benzene. The coloration phenomenon is usually interpreted as a consequence of the formation of a compound of the components. We consider such an explanation entirely probable in the given case, since very considerable changes occur in the spectrum.

The distance between the short-wave boundary of the absorption band of tetranitromethane and the most intense coloration of its mixtures with benzene amounts to about 100-110 mμ according to our data (Fig. 8). A distance of about the same order of magnitude (∼ 180 mμ) exists between the maximum absorption of the vapors of tetranitromethane [6] and of a solution of its mixture with benzene in carbon tetrachloride [1]. In spite of the approximate evaluation of the positions of the absorption bands, it can be concluded that significant energetic changes in the component molecules, associated with changes in their structure, occur in the system.

During dilution of mixtures of tetranitromethane and benzene with carbon tetrachloride, the optical density

rapidly falls, and does not obey the Lambert-Beer law, and the position of the maximum on the D – N curves is changed, approaching a molar component ratio of 1:1.

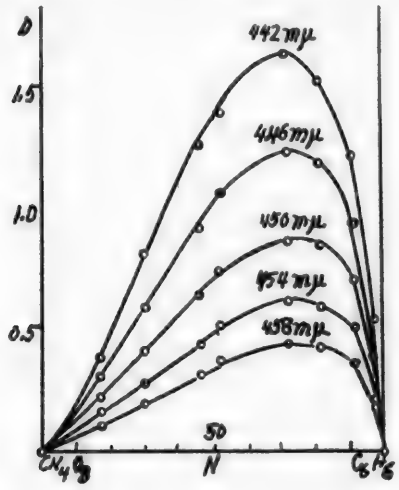

Fig. 7. Optical density (D), as a function of the composition of mixtures of tetranitromethane and benzene (in mol.%.

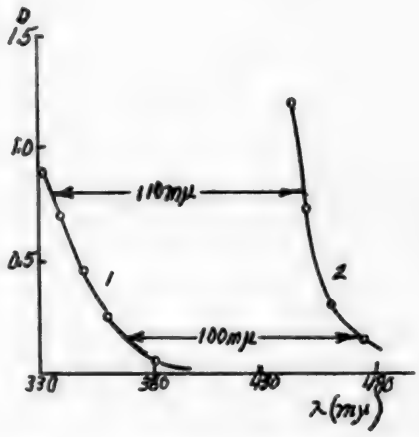

Fig. 8. Short-wave boundary of the absorption band of tetranitromethane (1) and mixtures of 72 mol.% $C(NO_2)_4$ + 28 mol % C_6H_6 (2).

The spectrophotometric measurements thus render very probable the hypothesis concerning the formation in the system: tetranitromethane – benzene of compounds of the components which are decomposed during dilution with a third component.

It is very interesting that the hypothetical compounds did not appear on one of the other property – composition diagrams studied by us. This fact, in all probability, is to be explained by the extraordinary instability of the complexes being formed and their very low concentrations in the system.

Hammick and co-workers [1] evaluated the concentration of the complex as being of the order of 10^{-4} moles/liter (in molar solution) on the basis of spectrophotometric study of solutions of $C(NO_2)_4$ and benzene in CCl_4. It is natural that admixture of such a small quantity of compound would not be appreciably reflected on the isotherms of many of the properties of the system.

The great sensitivity of the spectrophotometric method in the given case should by no means be interpreted in the sense either of its universality or of an exclusive position for it among other physico-chemical analytical methods. There is nc doubt that a profound and complete representation of the behavior of the components in solutions can be obtained only by complex investigation by various methods. However, for this purpose it is impossible to limit oneself to the traditional comparison of the form of the property–composition curves with the empirically established types of the isotherms and their classifications. Such a purely phenomenological method without knowledge of the quantitative laws determining the forms of the isotherms of each property can readily lead to erroneous conclusions, even if certain properties of the system are investigated.

In this connection the spectrophotometric and refractrometric data in the system under study were compared. It would appear that the close physical relation between the phenomena of absorption and refraction of light would have permitted one to expect a correspondence in the results of these methods; however, the formally described interpretation of the form of the refractive index isotherm leads to results directly opposed to the spectrum data. The curves $\underline{n}\lambda - V$, convex toward the composition axis, become less curved in proportion as they approach the violet end of the spectrum and approach the straight line form of the isotherm of an ideal system. Thus, the deviations from additivity which are considered in physico-chemical analysis as a criterion of an ideal system, in the given case diminish exactly in proportion as one approaches the region of the spectrum where reaction of the components appears particularly distinct (see Figs. 6 and 7). The explanation of this can only be given on the basis of the quantitative study of the various factors which influence the form of the isotherm $\underline{n}(V)$, to which it is proposed to devote a special investigation. It is evident from the example set forth that the position of the absorption band can not be considered a prime factor determining the form of the isotherm $\underline{n}$ (V). Volume changes occurring in

the system exert a much stronger influence on it. In mixtures of $C(NO_2)_4$ with C_6H_6 the signs of $\Delta\underline{n}(V)$ and $\Delta\underline{v}(P)$ are usually found in agreement with the overwhelming majority of liquid systems [16, 17], in spite of the strong bathochromic displacement of the absorption band. This latter, acting in the direction opposed to the influence of expansion, only somewhat diminishes the absolute value of $\Delta\underline{n}(V)$, and does not change its sign.

SUMMARY

1. The thermal and viscosimetric methods of physico-chemical analysis do not give any indications of a chemical reaction in the system: tetranitromethane – benzene. The expansion observed in the system, the minimum of the surface tension and the negative deviation from additivity of the refractive index agree with this conclusion.

2. The optical density curves (at λ = 442-458mμ) have pronounced maxima which are evidence of a reaction of the components. The very great magnitude of the bathochromic displacement of the absorption band in the given system permits this to be interpreted as a consequence of the formation of unstable complexes. The absence of indications of complex formation on the curves of other physical properties should, apparently, be considered a result of the very low concentration of the complexes.

3. The lack of correspondence in the data of the spectrophotometric and refractometric methods of physico-chemical analysis even at the short-waves close to the absorption band, is evidence of the fact that the change in the absorption band is not the chief factor determining the form of the isotherms $\underline{n}(V)$.

4. The refractive dispersion displays a considerable positive deviation from additivity, passing through a maximum. The dispersion isotherms, thus do not repeat the form of the refractive index isotherms and merit a special study.

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STUDY OF THE REACTION OF 8-HYDROXYQUINOLINE WITH ORGANIC ACIDS BY THE METHODS OF PHYSICO-CHEMICAL ANALYSIS

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8-Hydroxyquinoline or oxine, synthesized for the first time in 1859 by Lyubavin [1], has attained great importance in analytical chemistry for the qualitative and quantitative separation of metals, with which it forms strong complex compounds [2]. Its chemical properties are of interest on account of the mutual influence of the heterocyclic nitrogen and the phenol group which are in the o-position to each other.

The separation of metals with the aid of 8-hydroxyquinoline is conducted in the presence of organic acids, but the reaction of 8-hydroxyquinoline with these acids has not been investigated.

We studied the systems formed by 8-hydroxyquinoline with acetic, benzoic and salicylic acids by the melting point, viscosity, density and electrical conductivity methods and with the melting point method, additionally studied the systems formed by 8-hydroxyquinoline with monochloroacetic, p-hydroxybenzoic, p-nitrobenzoic, cinnamic and hydrocinnamic acids.

The method of investigation was the same as in the preceding works [3]. The viscosity was expressed in centipoises, the concentration – in mole per cent.

The System 8-Hydroxyquinoline – Acetic Acid

Glacial acetic acid after repeated fractional crystallization and boiling with acetic anhydride was carefully purified and had a m.p. of 16.5°, a b.p. of 118°, d_4^{60} 1.0105. "Pure" brand 8-hydroxyquinoline was recrystallized several times from ethyl alcohol, m.p. 75°, d_4^{80} 1.1594.

The results of the melting point measurements are presented on Fig. 1.

The melting point curve consists of two branches. We did not succeed in producing crystallization in the section from 25 to 10 mole %. There is a maximum on the viscosity isotherm η (Fig. 2) corresponding to 35 mole % of 8-hydroxyquinoline which partially explains the formation of glasses in the solid phase. The viscosity isotherm is convex toward the composition axis in the section from 100 to 60 mole %, which is evidence of the decomposition of acetic acid dimers. There is a maximum on the curve of the temperature coefficient of viscosity γ which corresponds to 35 mole % of 8-hydroxyquinoline. This is evidence of the fact that a compound with a component ratio 1:2 of the composition $C_9H_7NO \cdot 2CH_3COOH$ is formed in the liquid phase. There are pronounced maxima on the electrical conductivity isotherms κ (Fig. 3) which correspond

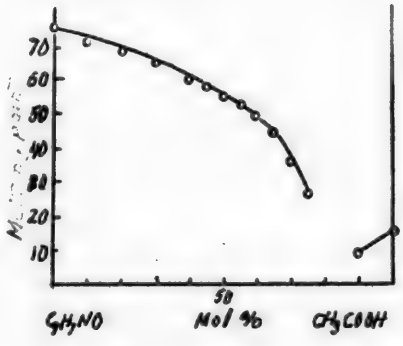

Fig. 1.

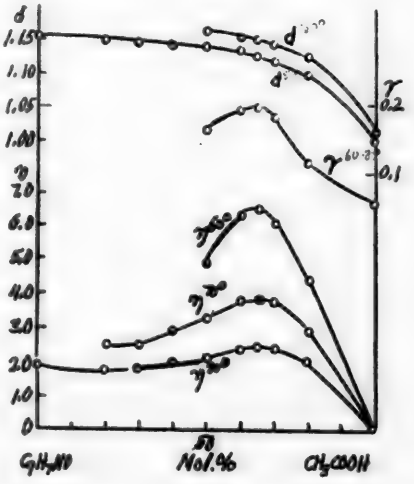

Fig. 2.

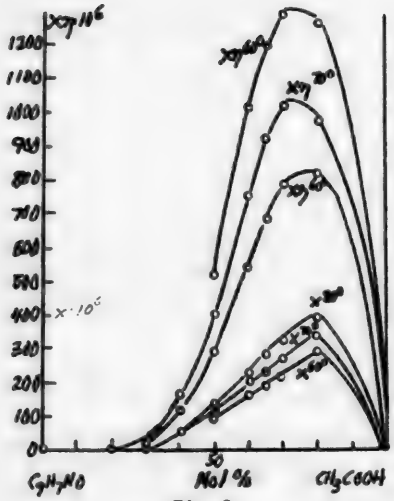

Fig. 3.

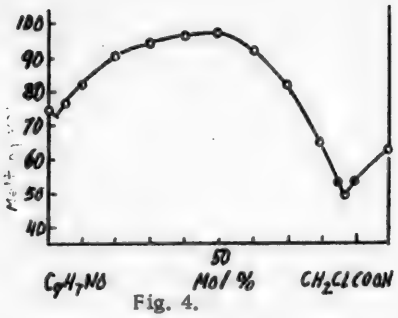

Fig. 4.

to 20 mole % of 8-hydroxyquinoline. By correcting the electrical conductivity for the viscosity $\kappa\eta$, the maxima on the curves are displaced by approximately 30 mole % of 8-hydroxyquinoline, which also confirms the formation of a compound $C_9H_7NO \cdot 2CH_3COOH$ in the liquid phase.

The System: 8-Hydroxyquinoline – Monochloroacetic Acid

Monochloroacetic acid was purified by distillation and was kept in sealed ampoules. It had m.p. 63° and b.p. 186.5°.

The results of the freezing point measurements of the given system are portrayed in Fig. 4. During the reaction of monochloroacetic acid with 8-hydroxyquinoline a compound is formed with a ratio of components of 1:1 of the composition $C_9H_7NO \cdot CH_2ClCOOH$, which corresponds to a maximum on the freezing point curve at 50 mole % of 8-hydroxyquinoline and m.p. of 98°, and also eutectic points. The first eutectic point with m.p. 73° corresponds to 89 mole % of 8-hydroxyquinoline, the second eutectic point with m.p. 49° corresponds to 30 mole % of 8-hydroxyquinoline. The maximum is diffuse which is evidence of dissociation of the compound during fusion. It was not

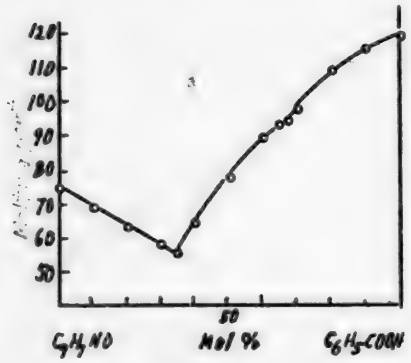

Fig. 5.

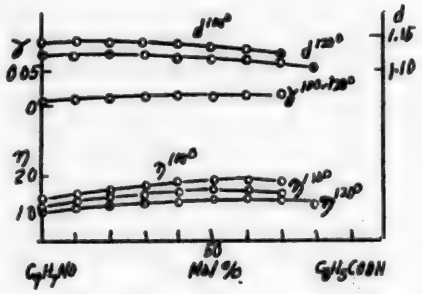

Fig. 6.

possible to take the isotherms of viscosity, density and electrical conductivity, since at 100° and higher the compound decomposed with evolution of bubbles of gas, and the decomposition products quickly polymerized into a thick mass.

The System: 8-Hydroxyquinoline – Benzoic Acid

Benzoic acid was purified by recrystallization from water with subsequent sublimation, and had m.p. 121.7° and b.p. 249°. The results of the melting point measurements are portrayed in Fig. 5. There is a eutectic point with m.p. 56° corresponding to 65 mole % of 8-hydroxyquinoline on the m.p. curve and a peritectic point corresponding to 33.3 mole % of 8-hydroxyquinoline with m.p. 95°. A compound with a ratio of components of 1:2 of the composition $C_9H_7NO \cdot 2C_6H_5COOH$ is evidently formed in the liquid phase and the peritectic point coincides with

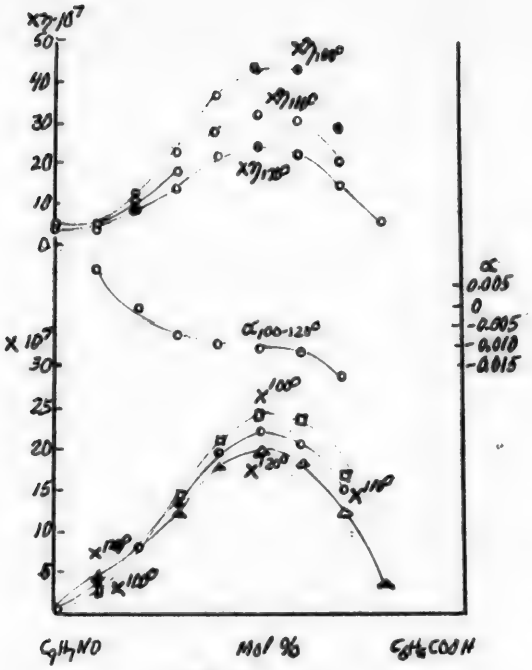

Fig. 7.

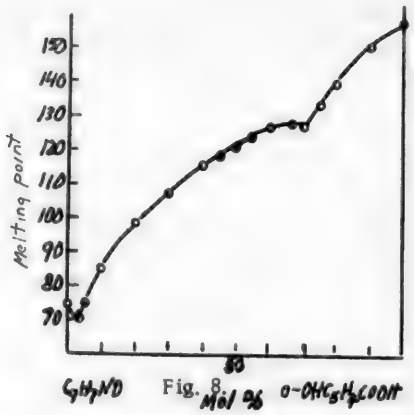

Fig. 8.

the maximum corresponding to the compound set forth above. We did not succeed in taking a cooling curve in view of the strong supercooling of the mixtures.

The viscosity isotherms (Fig. 6) are strongly flattened toward the composition axis; they have very diffuse maxima which correspond to 40 mole % of 8-hydroxyquinoline. There are no singular points on the curve of the temperature coefficient of viscosity γ (100-120°). The electrical conductivity isotherms consist of curves with a maximum corresponding to 50 mole % of 8-hydroxyquinoline (Fig. 7). Correcting the electrical conductivity for viscosity displaces the maximum on the curves to values of from 40 mole % of 8-hydroxyquinoline at 100° to 50 mole % of 8-hydroxyquinoline at 120°. The curve of the temperature coefficient of electrical conductivity a has an inflection point corresponding to 50 mole % of 8-hydroxyquinoline. On the section of the curve for from 80 to 20 mole % of 8-hydroxyquinoline the values of the temperature coefficient of electrical conductivity have a negative sign.

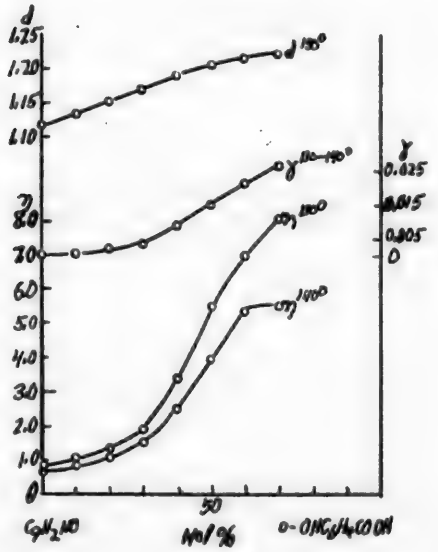

Fig. 9.

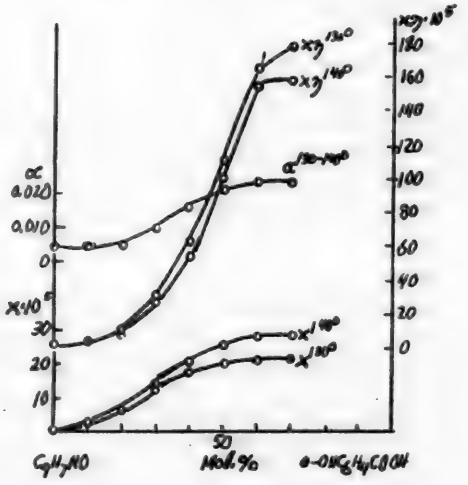

Fig. 10.

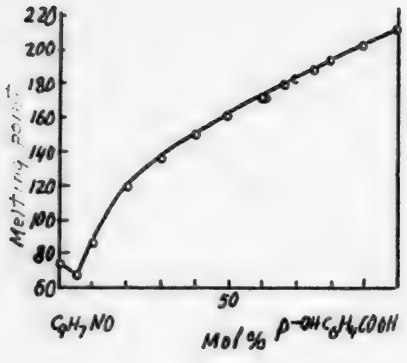

Fig. 11.

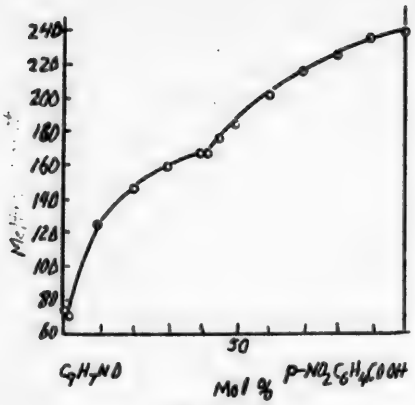

Fig. 12.

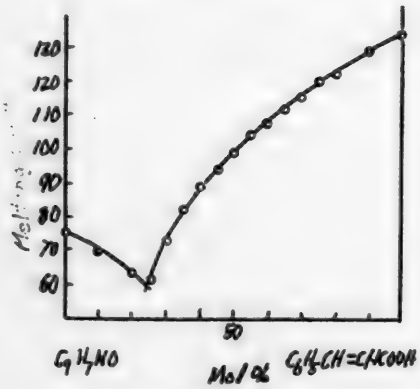

Fig. 13.

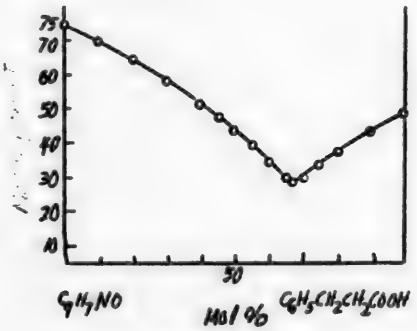

Fig. 14.

On the basis of the data obtained it can be assumed that a compound exists in the liquid phase, but in view of the low values of the magnitudes of the electrical conductivity, it is impossible to say anything definite concerning the composition of the compound.

The System: 8-Hydroxyquinoline – Salicylic Acid

"C.p." brand salicylic acid was carefully purified by repeated recrystallization and had m.p. 156°. The results of the melting point measurements are portrayed in Fig. 8. On the melting point curve there is a dystectic point with m.p. 127.5° and two eutectic points, which correspond 1) to 97 mole % of 8-hydroxyquinoline (m.p. 70°), and 2) to 29 mole % of 8-hydroxyquinoline (m.p. 126°).

The dystectic point corresponds to a compound of the composition

$$C_9H_7NO \cdot 2C_6H_4OHCOOH.$$

We were not entirely successful in recording the viscosity isotherms (Fig. 9), since during heating the mixtures above 140° evolution of gas bubbles is observed. The cut-off portions of the viscosity isotherms consist of S-shaped curves with an inflection point at 60 mole % of 8-hydroxyquinoline.

The curve of the temperature coefficient of viscosity γ repeats the course of the viscosity isotherm. The form of the isotherm is evidence of the fact that there is a chemical compound between the components in the liquid phase. The electrical conductivity isotherms (Fig. 10) have an S-shaped form with an inflection point at 80 mole % of 8-hydroxyquinoline. The character of the curves is not changed by correcting the electrical conductivity for viscosity.

The System: 8-Hydroxyquinoline – p-Hydroxybenzoic Acid

p-Hydroxybenzoic acid was purified by recrystallization from ethyl alcohol and had m.p. 219°. The melting point curve (Fig. 11) consisted of two branches intersecting in a eutectic point which corresponded to 6 mole % of 8-hydroxyquinoline and had m.p. 67°. Judging by the form of the melting point curve, there was no reaction between the components.

The System: 8-Hydroxyquinoline – p-Nitrobenzoic Acid

"C.p." brand p-nitrobenzoic acid had m.p. 238°. The results of the melting point measurements are portrayed in Fig. 12.

On the melting point curve there is a eutectic point corresponding to 99 mole % of 8-hydroxyquinoline (m.p. 72°) and a peritectic point, corresponding to 58 mole % of 8-hydroxyquinoline (m.p. 168.5°). A compound with an incongruent melting point is formed by reaction between the components.

The System: 8-Hydroxyquinoline – Cinnamic Acid

"C.p." brand cinnamic acid had m.p. 134° and b.p. 300°. The melting point curve (Fig. 13) consisted of two branches intersecting at a eutectic point which corresponds to 70 mole % of 8-hydroxyquinoline (m.p. 60°). No reaction between the components was detected.

The System: 8-Hydroxyquinoline – Hydrocinnamic Acid

"C.p." brand hydrocinnamic acid was recrystallized from alcohol and had m.p. 49° and b.p. 279.5°. The melting point curve (Fig. 14) consisted of two branches intersecting in a eutectic point which corresponded to 32 mole % of 8-hydroxyquinoline (m.p. 28.5°). There was no reaction between the components.

DISCUSSION OF RESULTS

8-Hydroxyquinoline containing a heterocyclic nitrogen atom and a hydroxyl group, can, depending on the nature of the substance reacting with it, assume either a basic or an acidic character. When reacting with a substance of an acidic character, the 8-hydroxyquinoline displays basic properties. Thus, by reaction of 8-hydroxyquinoline with acetic acid a compound of the composition 1:2 (two molecules of acid) is formed.

During the addition of acetic acid to 8-hydroxyquinoline, decomposition of its dimers occurs and is reflected in the viscosity isotherms; it is the monomers of acetic acid which react with the 8-hydroxyquinoline.

The activity of acetic acid is increased by the introduction of chlorine into the molecule. A compound of the composition 1:1 detected by the melting point method in the given system was possibly formed in an acid-base reaction. In the system: 8-hydroxyquinoline – hydroxybenzoic acid, as well as in the system with acetic acid, a compound of the composition 1:2 was detected. The introduction into the molecule of benzoic acid of a hydroxyl group in the ortho position, increases its acidic properties, and one could expect an increase in the activity of the reaction of 8-hydroxyquinoline with salicyclic acid.

Actually, a compound with a congruent melting point with a composition of 1:2 was detected in this system by the melting point method. But chemical reaction between the components was not detected during the introduction of a hydroxyl group into benzoic acid. If one introduces the nitrogroup into the benzoic acid molecule in the para-position, then its activity with respect to 8-hydroxyquinoline is partially increased, and a compound with an incongruent melting point is successfully shown in the system: 8-hydroxyquinoline – p-nitrobenzoic acid by the melting point method.

Reaction was not detected in the systems: 8-hydroxyquinoline – cinnamic and hydrocinnamic acids.

SUMMARY

1. With acetic, monochloroacetic, benzoic and salicylic acids 8-hydroxyquinoline forms compounds of the composition: $C_9H_7NO \cdot 2CH_3COOH$, $C_9H_7NO \cdot CH_2ClCOOH$, $C_9H_7NO \cdot 2C_6H_5COOH$ and $C_9H_7NO \cdot 2C_6H_4OHCOOH$.

2. 8-Hydroxyquinoline forms a compound with an incongruent melting point with p-nitrobenzoic acid.

3. 8-Hydroxyquinoline does not react with p-hydroxybenzoic, cinnamic or hydrocinnamic acids.

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* See Consultants Bureau Translation, page 2143

ALKYLATION OF AROMATIC HYDROCARBONS WITH OLEFINS IN THE PRESENCE OF METALLIC ALUMINUM AND HALOGEN DERIVATIVES

N. G. Sidorova, I. P. Tsukervanik and E. Pak

In a preceding communication [1], the condensation reaction of halogen derivatives with aromatic hydrocarbons in the presence of metallic aluminum, pioneered by Radziwanowski [2] and later studied by Azatyan [3], was studied by us. We accomplished the condensation of a number of chlorine (and partially of bromine) alkyls with benzene and toluene. We obtained the following yields of monoalkylated hydrocarbons by this route: ethylbenzene 74%; sec.-butylbenzene 81%; sec.-butyltoluene 64%; isoamylbenzene 66%; sec.-octylbenzene 47%; and diphenylmethane 70% of the theoretical. This method of synthesis is simpler and better for diphenylmethane than that known in the literature [4].

This method of preparing alkylbenzenes has great advantages as compared with the classical synthesis of Gustavson–Friedel–Crafts. It was natural to attempt to extend it to the alkylation of aromatic hydrocarbons with olefins. During the alkylation of halogen derivatives, they initially form halogen aluminates with metallic aluminum, which subsequently induce condensation of alkyl halides with aromatic hydrocarbons. The addition of some extraneous substance capable of yielding $AlCl_3$ or $AlBr_3$ with metallic aluminum was necessary for alkylation with olefins. Either hydrogen chloride, employed for the first time by Radziwanowski [2] in the condensation reactions of halogen derivatives with aromatic hydrocarbons in the presence of aluminum or bromine recently utilized in such syntheses [5] could serve as such additions. Such catalysts have not been employed by anyone for the alkylation of olefins.

We employed halogen derivatives as additives. The role of the halogen derivatives was twofold in this case: they serve for the preparation of $AlCl_3$ and are alkylating substances. Such a variation in the alkylation is even more efficient than the condensation of alkyl halides with aromatic hydrocarbons in the presence of metallic aluminum. Here we replace the greater part of the expensive halogen derivatives with the cheap olefins.

We studied the alkylation of benzene by ethylene, propylene, isobutylene, isoamylene and cyclohexene. As addition agent we used (mostly) the alkyl halide (chiefly the chloride) corresponding to the olefins. The quantity of aluminum employed does not have great significance, since only a small part of it enters into the reaction.

All the reactions gave a positive result. The yields of monoalkylated hydrocarbons amounted to 40-71% of the theoretical calculating on the basis of the olefin entering into the reaction and the alkyl halide taken. The reaction proceeds very well with the low molecular weight olefins at room temperature, but with increase in the molecular weight of the olefin a higher temperature is required. We noted in addition that the bulk of the olefin did not react during very energetic stirring. We therefore conducted all the subsequent experiments with moderate stirring and slow passage of the olefin. More complete absorption of the olefin proceeded in this case.

EXPERIMENTAL

The metallic aluminum necessary for the reaction was rapidly rubbed with a file into the form of a coarse powder and immediately drenched with benzene to protect it from oxidation by atmospheric oxygen.

All the olefins used in the condensations were prepared by dehydrogenation of alcohols over aluminum oxide.

The reactions were conducted in a three-necked flask with a reflux condenser, a thermometer and a tube for supplying the olefin. The gaseous olefins were admitted into the reaction from a gas holder after having been preliminarily conducted through a tall calcium chloride column. In the case of isoamylene and cyclohexene, in place of this tube, a dropping funnel was substituted, by the aid of which a solution of the olefin in an aromatic

hydrocarbon was added. The end of the condenser was joined, through a calcium chloride tube and a Tishchenko bottle, with a second gas holder to collect the unreacted olefin. It was necessary to clean the apparatus carefully, since otherwise the reaction could either not proceed or could only begin after prolonged heating of the mixture.

The order of conducting the condensations was the same in all the experiments. The mixture of benzene, halogen derivative and metallic aluminum was heated at the boiling temperature until the reaction began, which was noted by the evolution of hydrogen chloride and darkening of the mixture. After this the needed temperature was established and the olefin was released at such a rate that the bubbles could be counted. The mixture was then usually left to stand until the following day, after which decomposition with water and acidification with hydrochloric acid was carried out. The hydrocarbon layer was separated, washed with water, dried over calcium chloride and fractionated. The hydrocarbons obtained were again redistilled over sodium. The excess benzene was used again after purification.

The condensations which gave the best results are summarized in Table 1. The physical properties of the hydrocarbons prepared are summarized in Table 2.

TABLE 1

Results of the Condensation of Olefins with Benzene

Starting materials				Temperature (in °)	Yield of products	
Olefin (in liters)	Benzene (in g)	Halogen derivative (in g)	Aluminum (in g)		Monoalkylated (in g)	Di- and polyalkylated (g)
Ethylene 2.0	120	n-C_4H_9C 13.3	0.1	20-30	4.2 (47.7%)	1
Propylene 3.0	100	iso-C_3H_7Br 3.5	0.15	20-23	13.0 (71%)	2.5
Isobutylene 4.0	100	n-C_4H_9Cl 3.7	0.2	40-45	10.7 (40%)	8
Isoamylene 8.2 g . . .	50	iso-$C_5H_{11}Cl$ 1.85	0.2	75-80	9.0 (45.5%)	0.9
Cyclohexene 8.2 g . .	60	n-C_4H_9Cl 1.0	0.1	60	7.0 (41%)	3.0

TABLE 2

Physical Properties of the Hydrocarbons

Hydrocarbon	Boiling point	d_4^{20}	n_D^{20}	Found MR_D	Calculated MR_D
Ethylbenzene	134° (725 mm)	0.8664	1.4957	35.75	35.55
Isopropylbenzene	150-150.5 (725 mm)	0.8630	1.4899	40.19	40.17
tert.-Butylbenzene	165-166 (725 mm)	0.8670	1.4907	44.78	44.79
tert.-Amylbenzene	186-187 (725 mm)	0.8648	1.4904	49.56	49.41
Phenylcyclohexane	233-235 (722 mm)	0.9428	1.5228	51.87	51.82

SUMMARY

The possibility was demonstrated of alkylating aromatic hydrocarbons with olefins in the presence of metallic aluminum with the addition of halogen derivatives. The yield of monoalkylated hydrocarbons amounted to 40-71% of the theoretical.

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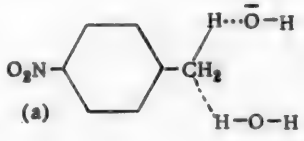
INVESTIGATION OF THE MIGRATION ROUTES OF THE HYDROGEN ATOM DURING CERTAIN OXIDATION-REDUCTION REACTIONS. I

A. F. Rekasheva and G. P. Miklukhin

The covalent bond can be cleaved either with the formation of two neutral radicals, each of which retains one electron of the bond pair, or with the formation of two ions, one of which retains both electrons. The first type of bond cleavage is called homolytic or radical; the second – heterolytic or ionic [1].

Homolysis of bonds is energetically more efficient for any given molecule than heterolysis, since during the latter process it is necessary to expend additional energy to separate the charged ions. For this reason the majority of gaseous reactions are of the atomic or homolytic type. In solutions, however, it is necessary to take into account the electrostatic reaction of the molecules of the reacting substances with the solvent, which not only lowers the electrostatic work of separating the ions in the moment of the reaction, but also extends the polar bond prior to the act of reaction of either compound. It is precisely on this account that the majority of reactions in solutions have an ionic mechanism, i.e., proceed with heterolysis of the bonds.

Specification of an ionic cleavage mechanism does not mean an obligatory formation of free ions in solution. We can refer to the exchange reaction between 2-nitrotoluene and heavy water [2] as an example. This process certainly has an ionic mechanism; we do not, however, suppose that ions of 2-nitrotoluene actually exist in solution. In all probability, the reaction proceeds due to the formation of complexes between water, nitrotoluene and a catalyzing base, for example (a).



(a)

Exactly such a process was proposed in the works of A. I. Shatenshtein and coworkers [3] who were studying the exchange reactions of hydrocarbons with liquid deuterio-ammonia.

We consider the actual formation of free radicals as entirely non-obligatory, just as in the case of the homolytic cleavage of bonds. In what follows we shall speak of the radical or ionic cleavage of bonds, of their homolysis and heterolysis, without linking these phenomena with the question of the presence of free radicals or ions in the reaction mixtures.

It has long been known that the method of labeled atoms, along with the kinetic, spectrum and others, is one of the most important methods for the study of the mechanisms of chemical reactions [4-7]. There is, moreover, a whole series of questions for the resolution of which this method is unique. In particular, only with the aid of the labeled atom method can the route of migration of various atoms of either compound in various reactions be established without any reliance on analogy.

It is precisely this latter question concerning the routes of migration of atoms in reactions to which the several investigations, the results of which are summarized in this communication, are dedicated.

It is necessary to underline here the basic premises of this series of our works. In all probability, the question of bond strength should play a subordinate role in the consideration of ionic processes. Hydrogen entering into the composition of compounds in bonds such as that with oxygen exchanges very rapidly, while in bonds with carbon the exchange of hydrogen atoms proceeds, on the contrary, very slowly. At the same time, the O–H bond is considerably stronger than the C–H bond. Consequently, in ionic exchanges and, in all probability, in all other reactions it is not the strength of the bonds that determines the direction of the reaction. As was demonstrated by Brodsky [8] and confirmed in his works with Sulima and Khaskina [9, 10], exchange reactions proceed rapidly under conditions in which the atoms linked with the exchanging hydrogen have free electron pairs (nitrogen in NH_3,

oxygen in H_2O, etc.). We have already expressed the hypothesis in other works that ionic reactions are realized, in all probability, at the expense of cleavage of the most polar bonds [29].

During homolytic processes• the situation should be reversed: the polar bonds play no role; the course of the reaction is determined by the strength of the bonds. If this basic position is correct, then in a case when compounds containing hydrogen in O—H and C—H bonds are present in the reaction mixture, the hydrogen of the C—H bonds, as the least strong, should react in homolytic processes. This assumption could only be demonstrated with the aid of an isotopic method which permitted the substitution of the hydrogen of the O—H, C—H and other bonds and the elucidation of the routes of its migration during the reactions.••

Prior to our works several processes in which migration of the usually non-labile hydrogen atoms of the C—H bonds occurred had already been studied. Thus, during the Canizzaro reaction [11] the formation of alcohol was established by way of the direct migration of hydrogen from the C—H bond of one molecule of aldehyde to the C—H bond of another. During the electrolysis of salts of fatty acids, the radicals being formed during the disproportionation, transfer hydrogen atoms directly to each other without the participation of other molecules [12]. The methane evolved during the electrolysis of heavy acetic acid CD_3COOH in ordinary water has a composition CD_4, i.e., the methyl radical CD_3 formed from the acid, captures deuterium from other acid molecules, but not hydrogen from the solvent [13]. Further, during the reaction of formaldehyde with hydrogen peroxide in heavy water, light water is evolved, which is evidence of the direct joining of two hydrogen atoms originating from two formaldehyde molecules [14]. It has recently been demonstrated that a similar homolytic process takes place also during the decomposition of the peroxides of organic acids [15]. Finally, G. A. Razuvaev, G. G. Petukhov and the authors [16] have demonstrated that during the photoreaction of phenylmercury hydroxide with methyl or ethyl alcohols containing deuterium in the hydroxyl group, light benzene is formed, which is evidence of the capture by the phenyl residue of ordinary water from the C—H bonds of the alcohol, and not deuterium from its O—H bond.

We selected the reduction reaction of diazonium salts and aldehydes as the subject of the investigation, since there are indications suggesting that these processes are probably of a homolytic character [1, 17].

Reduction of Diazonium Salts with Ethyl Alcohol

The reduction of diazonium salts by ethyl alcohol is one of the most studied and widely applied methods of removing the amino group [18]. We studied the deamination reaction with ethyl alcohol containing deuterium in the hydroxyl group.••• The object of the work was to establish the source of the hydrogen which is transferred to the hydrocarbon from the alcohol. It is evident that both the hydrogen of the O—H bond of the alcohol, and the hydrogen of its C—H bond can participate in the reaction. The mechanism of the reaction of deamination with alcohols has never been investigated from this point of view. Until very recently, hypotheses have been advanced in the literature in accordance with which the hydrogen atoms migrate to the hydrocarbon from the O—H-groups of the alcohol [20].

Dry p-nitro- and m-chlorophenyldiazonium chlorides were prepared by the diazotization of the hydrochlorides of the corresponding amines with isobutylnitrite in absolute alcohol. After precipitation and washing the diazonium salts with absolute ether, they were quickly pressed out on filter paper and placed in absolute ethyl alcohol containing deuterium in the hydroxyl group and cooled to 0°. The latter was prepared by addition of deuterium oxide to absolute ethyl alcohol. After 24 hours a calculated quantity of metallic sodium (10% excess) was added to the alcohol, and the mixture, protected from moisture with a calcium chloride tube, was fractionated with a good fractionating column. The heavy ethyl alcohol was collected within limits of 0.3°.

The mixture of dry diazonium salts with heavy ethyl alcohol was very slowly heated to the boiling point in a flask supplied with a condenser and a calcium chloride tube. A very violent reaction course was observed in several experiments with ejection of a portion of the reaction mixture through the condenser. After completion of the reaction the basic mass of the alcohol was slowly distilled off, and the benzene derivatives were separated from the residue by steam distillation, dried and fractionated. Nitrobenzene was collected within the range of 209-211°, chlorobenzene boiled at 129-131° (756 mm).

• We denote a process homolytic or heterolytic if the stage of the reaction of interest to us—the migration of hydrogen—proceeds respectively with homolysis or heterolysis.

•• The complete absence of substantiated experimental data concerning the role of the hydride ions H^- in reactions of organic compounds permits us to ignore mechanisms involving them with reference to the processes under study.

••• A brief communication concerning this investigation was published earlier [19].

The alcohol was purified by repeated distillation, finally over calcium oxide and with the addition of metallic sodium. The fraction was collected which had b.p. 78-78.5°, n_D^{22} 1.3608-1.3615.

The purified benzene derivatives and the alcohol were burned over cupric oxide in a stream of dry air, and the water from the combustion was analyzed for its dueterium content by the flotation method. In contrast with the procedure ordinarily employed [18], with the object of economizing deuterium, we did not use a large excess of alcohol (30-40 ml of heavy ethyl alcohol for the quantity of diazonium salt obtained from 0.1 mole of the starting amine were taken for the reaction). In connection with this, the yields of benzene derivatives were small: they amounted to 30-40% for nitrobenzene, and 25-35% for chlorobenzene, calculated in each case on the basis of the amount of amine.

The deamination of 3-nitro-4-aminotoluene was conducted in a water-alcohol solution [21]. A solution of 16 g of amine in 50-70 ml of ordinary alcohol was mixed with 24 g of concentrated sulfuric acid (Sp. gr. 1.83) and diazotized with a solution of 8.2 g of sodium nitrite in 10 ml of deuterium oxide (6000γ). The alcohol was distilled off with a fractionating column and purified as described above. 3-Nitrotoluene was isolated from the residue after distilling off the alcohol by steam distillation. The purified dry benzene derivative and the alcohol were burned, and the density of the water of combustion was determined by the usual method. The results of the experiments are summarized in Table 1.

TABLE 1

Benzene derivative obtained	Deuterium content (in γ)			
	in the water from the combustion of ethyl alcohol	in the hydroxyl group of the ethyl alcohol	in the water from the combustion of the benzene derivative	
			Found	Calculated
Nitrobenzene	410	2460	21	490
	445	2670	9	535
	440	2640	26	530
	—	—	11	—
Chlorobenzene	380	2280	24	455
	370	2220	11	445
3-Nitrotoluene	560	3360	17	480
	630	3780	5	540

During the combustion of the organic compound (over cupric oxide in a stream of dry air), the deuterium present in some position of the molecule, is diluted by the rest of the hydrogen contained in the molecule. Knowing the deuterium content in the water from the combustion of the alcohol, one can readily calculate its content in the hydroxyl group of the alcohol prior to combustion: it is 6 times greater since the ethyl alcohol molecule contains 6 hydrogen atoms. These quantities are set forth in the third column of Table 1.

If the diazo group of the diazonium salts had been substituted during the reduction by the hydrogen of the hydroxyl group of the alcohol, then the deuterium content in that position of the benzene derivative which was previously occupied by the diazo group should have corresponded to the deuterium content of the hydroxyl group of the ethyl alcohol. The quantity of deuterium in the water of combustion of the given benzene derivative would be as many times less as the deuterium is diluted by hydrogen during the combustion. If there are m hydrogen atoms in the molecule of the benzene derivative, and the content of deuterium in the hydroxyl group of the ethyl alcohol amounts to A, then the content of deuterium in the water from the combustion of the hydrocarbon should be equal to A/m, if the hydrogen of the OH group of the alcohol participates in its formation. The numbers obtained by such a calculation are set forth in the last column of Table 1. Comparison of these quantities with those found experimentally convinces one of the fact that during the reduction of the diazonium salts by ethyl alcohol, hydrogen atoms are transferred to the benzene derivative being formed not from the OH group but from the CH bonds of the reducing agent. The small amount of heavy water in the water of combustion is to be explained both by contamination of the hydrocarbons with small quantities of organic compounds capable of exchanging their hydrogen atoms with the deuterium of the alcohol under the conditions of the experiments (for example, phenyl ethers [22]), and by the difficulty of purifying the analyzed samples of water from the last traces of foreign substances. The errors in measurement amount to 10-15γ, ordinarily in the direction of overstatement.

Thus, the benzene derivatives isolated by us practically do not contain deuterium. Consequently, hydrogen atoms of the CH bonds of the alcohol participate in the formation of benzene derivatives during the reduction of

diazonium salts with ethyl alcohol. Taking into account that the diazonium salts are reduced by such alcohols as benzyl, it can be assumed that the hydrogen is in all cases cleaved from the α-carbon atom of the alcohols, and, consequently, the reduction reaction can be portrayed by the scheme:

$$RN_2Cl + CH_3CH_2OD \longrightarrow RH + N_2 + DCl + CH_3CHO.$$

Investigation of the mechanism of a reaction by a single method very rarely can lead to the detailed solution of a problem. It is natural that in the given case a more detailed elucidation of the reaction mechanism of the deamination of diazonium salts by alcohols is not possible on the basis of the data obtained.

Reduction of Diazonium Salts by Hypophosphorous Acid

The deamination reaction was also studied by us using hypophosphorous acid as the reducing agent.* The possibility of reducing diazonium salts with hypophosphorous acid was demonstrated 50 years ago [23], and this method of deamination has been widely disseminated since then [18].

However, with the exception of a few investigations of the last few years, parctically nothing has been done to elucidate the mechanism of this reaction. There exists indirect evidence that this reaction of diazonium salt reduction proceeds by a chain mechanism with the participation of free radicals [24]. The authors of that investigation assumed that during the reaction hydrocarbon radicals are joined with hydrogen atoms and bound with the hypophosphorous acid through the phosphorus and not through oxygen, but no evidence whatsoever for this assumption was adduced.

Resolution of the question of how the hydrogen atoms of the hypophosphorous acid transfer to the hydrocarbon during the reduction of its diazonium salts is complicated first of all by the fact that, as Brodsky and Sulima [25] showed, hypophosphorous acid comparatively rapidly exchanges hydrogen atoms of the P—H bonds with the deuterium of heavy water. A second difficulty consists of the fact that in the reaction under investigation, as in a number of others, the rates of exchange of hydrogen and deuterium are variable.

The experimental data obtained by us demonstrate that the exchange reaction between the hydrogen atoms of water and the hydrogen atoms of the P—H bonds of hypophosphorous acid proceeds more slowly than the reduction reaction, particularly if the latter is conducted in the presence of catalyst (cupric sulfate). In the latter case the deamination process is successfully completed for the basic mass of diazonium salt before a considerable quantity of hypophosphorous acid molecules with deuterium in the P—H bonds appears in the mixture.

We should dwell in somewhat greater detail on the question of the fact that the rates of transfer of hydrogen and of deuterium do not coincide. This phenomenon was long ago detected for certain reactions [27]. It depends on the fact that rupture of the bond: element—deuterium requires greater activation energy than the rupture of the corresponding bond: element—hydrogen. In reversible reactions, for example, during the ordinary exchange reactions of hydrogen isotopes [4, 5] or during the distribution of deuterium between light and heavy benzene in the presence of aluminum chloride [28], this difference in the equilibrium distribution of hydrogen and deuterium is not important, since toward the moment of reaching the equilibrium state, hydrogen and deuterium manage to be distributed equally between the participants in the process and migrate reversibly from one compound to the other. However, during irreversible processes, when the hydrogen and deuterium atoms can transfer only in one direction, a comparatively smaller quantity of that isotope which is more strongly bound to the molecule participates in the reaction. Its concentration in the reaction product will be lower than would be expected if analgous bonds of both isotopes were equivalent. In a given case—the reduction, for example, of p-toluyldiazonium chloride by hypophosphorous acid, there was shown to be 3-4 times less deuterium in the para-position of the toluene obtained than there was in the P—H bonds of the reducing acid.** Consequently, in the water from the combustion of this toluene, 24-32 times less deuterium is contained than in the P—H bonds of hypophosphorous acid. In connection with this, it was necessary to work at very high dilution with the starting compounds concentrated in deuterium, and all the relative errors of measurement were greater than usual.

We describe a typical reduction experiment. p-Toluidine (11 g) in an alcoholic solution was saturated with dry hydrogen chloride and diazotized with butyl nitrite. The crystalline diazonium salt precipitated with ether was filtered off, washed with ether and dissolved in water. An approximately 55% solution of hypophosphorous

*A brief communication was published previously [30].

**Similar magnitudes were obtained by Alexander and Burge [26]. We became aware of this work only after our basic experiments had been conducted.

acid* was slowly added to the solution of diazonium salt at a temperature of −5 to +5°. After 24 hours the toluene formed was extracted from the reaction mixture with ether, washed with a solution of sodium hydroxide and then with water, dried with metallic sodium and fractionated. The toluene boiled over a range of 0.5°; n_D^{20} 1.4940-1.4957.** The purified toluene was burned over cupric oxide and the water from the combustion was analyzed for its deuterium content. The water from the reaction mixture after removing the toluene was distilled off in a vacuum and subjected to purification over incandescent cupric oxide, after which it was analyzed by the usual method. The results of the experiments are summarized in Table 2.

The goal of the present work was the elucidation of the source of the hydrogen transferred to the hydrocarbon during the reduction of the diazonium salts by hypophosphorous acid. If the hydrogen atoms of the P−H bonds of the acid were not exchanged for heavy water deuterium atoms, the question would be resolved simply: during the reduction of ordinary hypophosphorous acid dissolved in heavy water, the hydrocarbon being formed from the diazonium salt would not contain deuterium if the hydrogen of the P−H bonds reacted, and would contain deuterium if the hydrogen were transferred to the residue of the diazonium salt from the H−O bond of the acid. We studied such a reaction in the case of the reduction of diazonium salts by ethyl alcohol, in which the hydrogen of the C−H bond is not exchanged for the heavy water deuterium. On the other hand, if the hydrogen of the P−H bonds of hypophosphorous acid were instantly exchanged with the heavy water deuterium, then the problem formulated above could not in general be resolved, since there would be no distinction between the hydrogen atoms bound in the acid. However, if an exchange reaction occurs, but proceeds somewhat more slowly than the reduction reaction, choice between the O−H and P−H bonds of the reducing agent becomes possible. If P−H bond hydrogen is transferred to the diazonium salt radical, then during the reduction of the diazonium salt dissolved in heavy water by ordinary hypophosphorous acid, there should be considerably less deuterium in the hydrocarbon than during the reduction of diazonium salt dissolved in ordinary water by heavy hypophosphorous acid containing deuterium in the P−H bonds. This is natural since in the first case, it would primarily be hydrogen of the P−H bonds of the light acid and in the second case, primarily deuterium bound to the phosphorous in the heavy acid, that would be transferred to the hydrocarbon radical.

To aid in drawing quantitative conclusions concerning the source of the hydrogen which is transferred to the hydrocarbon we introduced the concept of the "% transfer of deuterium". Let us assume that the hydrogen of the P−H bonds of hypophosphorous acid instantaneously exchanges with the deuterium of the heavy water. In such a case it is not difficult to calculate how much deuterium there will be in the hydrocarbon obtained during the reaction, independently of whether the reduction is effected by light or heavy acid. It is evident that in this case there should be as great a portion of deuterium in the hydrocarbon as in the reaction mixture for the entire period during which the process proceeds ($d_{av.}$, Table 2). As a result of the difference in the rates of transfer of hydrogen and of deuterium to the hydrocarbon, while isotopic equilibrium is being established in the exchange reaction, i.e., during the reduction of heavy acid in heavy water, less deuterium is transferred, approximately 32% of the calculated value (Experiment 9, Table 2). This quantity, called by us "% transfer of deuterium" (last column, Table 2) is determined by dividing the experimentally found content of deuterium in one position of the hydrocarbon (d_h) by the average deuterium content in the reaction mixture ($d_{av.}$). As is evident from the data summarized in Table 2, during the reduction of diazonium salt dissolved in heavy water by ordinary hypophosphorous acid (in the presence of cupric sulfate, Experiments 10-12), considerably less deuterium is found in the hydrocarbon and the "% transfer" is reduced to 3-8%. On the other hand, during the reduction of diazonium salt dissolved in ordinary water by heavy hypophosphorous acid (Experiments 13-15), the "% transfer" becomes very high, reaching 200%.

These observations can only be explained by the fact that the above-indicated assumption concerning the possibility of instantaneous exchange of the hydrogen of the P−H bonds of hypophosphorous acid is erroneous. In actuality, these hydrogen atoms are exchanged more slowly than the rate at which the reduction reaction proceeds. In the first experiments (Experiments 10-12) the hydrocarbon is obtained primarily at the expense of the light hydrogen of the P−H bonds of hypophosphorous acid, which is not successfully exchanged for deuterium. On the other hand, in Experiments 13-15, the hydrocarbon is obtained primarily from the P−D bonds of the heavy hypophosphorous acid, which also is not successfully exchanged for the ordinary hydrogen of the water. Establishment of the fact of slow exchange of these hydrogen atoms which are transferred to the diazonium salt radical simultaneously resolves the question concerning the source of these hydrogen atoms, since it is well known that hydrogen

*The solution was obtained by saturating an aqueous solution of sodium hypophosphite with dry hydrogen chloride. The sodium chloride formed was filtered off. To obtain heavy hypophosphorous acid a known quantity of deuterium oxide was added to the solution and the mixture was left to stand at room temperature for a prolonged time.

**For various experiments. Apurer product which would have given a better yield in these experiments, could have been prepared.

TABLE 2

Reduction of p-Toluyldiazonium Chloride by Hypophosphorous Acid*

Experiment No.	Quantity of H_3PO_2 (in g)	Quantity and increment in density of water				Increment in density of water (in γ)			% transfer of deuterium
		for H_3PO_2 solution		for diazonium salt solution		in the mixture at the end of the reaction d_e	average $d_{av.}$	water from the combustion of the hydrocarbon $\cdot 8\, d_h$	
		(g)	(γ)	(g)	(γ)				
1	55	25	0	103	3100	2280	2690	370	14
2	61	27	0	90	3700	2540	3120	270	9
3a	61	27	0	90	3700	2540	3120	460	15
4b	91	57	3870	31	3700	3280	3490	430	12
5c	62	28	3860	22	2000	2380	2190	370	17
6	88	40	0	150	2000	1430	1710	185	11
								335	20
								410	24
7d	61	27	4320	20	1500	2410	1950	700	36
8e	46	21	4320	20	1500	2360	1930	810	42
9e	62	28	3940	75	3260	3030	3150	1000	32
10	61	27	0	100	2920	2070	2490	80	3
11	55	25	0	100	1720	1250	1480	120	8
12	66	30	0	100	2170	1500	1830	120	6
13	56	26	7970	75	0	1830	910	1640	180
14	56	26	3430	100	0	640	320	600	190
15	57	27	4930	60	0	1340	670	905	140

atoms entering into the O—H bond of hypophosphorous acid, as in any other compound [4, 5], instantaneously exchange with the deuterium of heavy water. Consequently, it is hydrogen atoms bound through the phosphorous of the hypophosphorous acid which are transferred to the hydrocarbon radical of the diazonium salt.

Three series of experiments were conducted. In the first series (Experiments 1-6) solutions of diazonium salts in heavy water were reduced with ordinary hypophosphorus acid or with hypophosphorous acid which had preliminarily been placed in contact with heavy water for a duration of 10-15 minutes in all. The results obtained are evidence of the fact that during such an experimental arrangement of experiments, the percent transfer of deuterium into toluene varies from 9 to 17. It is necessary to discuss the results of Experiment 6 separately. This experiment differed from the others in the fact that the toluene was not isolated all at once and as a whole from the reaction mixture after completion of the reaction, but in portions as the toluene was formed, in quantities sufficient for conducting analyses. Three samples of toluene in all were taken; the two last samples, as is evident from Table 2, contained more deuterium than the first. This is readily explained by the fact that the formation of toluene in the two last samples proceeded by means of reaction of the diazonium salt with hypophosphorous acid, which had already succeeded to a considerable extent in exchanging its hydrogen atoms of the P—H bonds for deuterium of the heavy water.

In the second series of experiments (Experiments 7-9) the solution of diazonium salt in heavy water was reduced with hypophosphorous acid which was preliminarily placed in contact with heavy water for a duration of many hours (from 47 to 96 hours) at room temperature. Comparison of the results obtained in the first series of

* a Temperature of the reaction mixture 35-45°.

Time of preliminary contact between the water and hypophosphorous acid:

b 10 minutes

c 15 minutes

d 47 hours

e 91 hours

In Experiment 6 the first sample was taken after 1 hour 50 minutes, the second after 3 hours 50 minutes, the third after 24 hours.

Experiments 9-15 were conducted in the presence of cupric sulfate; the remaining experiments — without catalyst.

experiments with the results of the second series shows that reduction of the diazonium salt with hypophosphorous acid placed for a prolonged period in contact with heavy water leads to an increase in the content of deuterium in the toluene being formed by a factor of almost two, in comparison with the toluene obtained by the reduction of diazonium salt with hypophosphorous acid not containing deuterium at the beginning of the reduction reaction or placed in contact with heavy water insufficiently long for substantial exchange of all the hydrogen atoms in the molecule.

In follows from this that the exchange of those hydrogen atoms of hypophosphorous acid which participate in the formation of the hydrocarbon does not proceed instantaneously, but at a rate not very markedly different from the rate of the reduction reaction.

For a still more definite clarification of the source of the hydrogen, it was evidently necessary to accelerate the reduction process without simultaneously accelerating the rate of the exchange reaction. Raising the reaction temperature did not bring this about.

We succeeded in achieving the desired result by catalyzing the reduction reaction with cupric sulfate [24]. The experiments of the third series (Experiments 9-15) were conducted analogously to the first two series but in the presence of catalyst. Toluene was extracted from the mixture 10 minutes after the beginning of the mixture of the reagents; the mixing process took about 5 minutes. The results obtained are evidence of the fact that during the addition of ordinary hypophosphorous acid to a solution of diazonium salt in heavy water in the presence of cupric sulfate (Experiments 10-12), toluene containing very little deuterium is formed. The percent of transfer of deuterium in this case is low, which is evidence of the fact that the bulk of the toluene is formed at the expense of the hydrogen of the P−H bonds of the hypophosphorous acid which has not succeeded in exchanging its hydrogen for the deuterium of the water. If the exchange had proceeded prior to the reduction reaction, then the percent transfer of deuterium would have been equal to approximately 30-35 (Experiment 9, Expts. 7 and 8 in part, Table 2 in which exchange does not complicate the picture). On the contrary, during the reduction of a solution of diazonium salt in ordinary water by heavy hypophosphorous acid (Experiments 13-15) the percent transfer of deuterium is very high, which is again evidence of the transfer to the toluene of deuterium from the heavy hypophosphorous acid which successfully exchanged the P−D bonds.

The results of the experiments, which are summarized in Table 2, permit us to make a rough computation of the ratio of the rates of exchange and of reduction. Let us assume that this ratio of rates amounts to:

$$\frac{V_{exch.}}{V_{red.}} = \frac{1}{n} .$$

It is readily seen that of $\underline{m}$ hypophosphorous acid molecules $\frac{m}{n+1}$ are exchanged prior to the act of reduction and reduce $\frac{n \cdot m}{n+1}$ molecules of diazonium salt without exchange, since the comparative rates of exchange and reduction are equal to $\frac{1}{n+1}$ and $\frac{n}{n+1}$, respectively. The average isotopic composition of the hydrogen of the hypophosphorous acid which is transferred to the hydrocarbon, $\underline{d}$ will be equal to

$$d = \frac{\frac{n \cdot m}{n+1} \cdot d_d + \frac{m}{n+1} \cdot \frac{d_w + d_e}{2}}{m}$$

or

$$d = \frac{n \cdot d_d + d_{av.}}{n+1}$$

where d_d is the initial deuterium content in the P−H bonds of hypophosphorous acid (the donor), d_w is the deuterium content in the water employed to dissolve the diazonium salt, d_e is the deuterium content in the final reaction mixture and $d_{av.}$ is half the sum of the values of d_w and d_e.

The percent transfer of deuterium if the exchange reaction is excluded is equal to 32 (Experiment 9). Taking this percent transfer of deuterium into account, it is readily found that there should be 0.32 d deuterium

TABLE 3

Experiment No.	Group	n
1	I	1.3
2		2.7
3		1.2
4		1.6
5		0.9
6		1.4
10	II	10.0(?)
11		3.0
12		3.9
13	III	1.4
14		1.0
15		1.0

in a single position of the hydrocarbon. Experimentally we find values equal to d_h (next to the last column of Table 2). This makes it clear that it is possible to construct an equation to determine n. It will have the form:

$$d_h = 0.32 \cdot d, \text{ or } d_h = 0.32 \cdot \frac{nd_d + d_{av.}}{n + 1} . \quad (I)$$

Placing the values for the density of water from Table 2 in formula (I), we find (in reduction with light hypophosphorous acid $d_d = 0$) quantities which are presented in Table 3.

It follows from these data that for the reduction reaction with light hypophosphorous acid without catalyst (Group I) the quantity n is on the average close to 1.5. For reduction with light hypophosphorous acid in the presence of cupric sulfate (Group II) n is close to 4 and for reduction with heavy hypophosphorous acid in the presence of cupric sulfate (Group III) n is slightly above 1. It is evident that these computations have only a tentative character; however, for all that, they apparently give the correct order of magnitude of the unknown quantities.

Consequently, in the absence of catalyst the rate of exchange is only a little less than the rate of reduction (approximately one and half times). However, in the presence of catalyst which accelerates the rate of reaction, the exchange proceeds considerably slower than the reduction (approximately 4 times). The reversible exchange reaction has a rate of the same order of magnitude as the rate of the reduction with heavy hypophosphorous acid.

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SUMMARY

1. The hydrogen of the C−H bonds of alcohol and of the P−H bonds of hypophosphorous acid was transferred to the hydrocarbon radical of diazonium salts.

2. Deuterium at the P−H bond of hypophosphorous acid is transferred to the compound being reduced approximately 3 times more slowly than hydrogen.

3. In the absence of catalyst the rate of exchange of hydrogen at the P−H bonds of hypophosphorous acid is somewhat less than the rate of reduction. In the presence of cupric sulfate the rate of reduction considerably increases and the exchange reaction proceeds approximately 4 times slower than the reduction reaction.

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INVESTIGATION OF THE MIGRATION ROUTES OF THE HYDROGEN ATOM DURING CERTAIN OXIDATION-REDUCTION REACTIONS. II

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In the preceding work [1] the results of our experiments on the reduction of diazonium salts with ethyl alcohol and hypophosphorous acid containing the heavy isotope of hydrogen—deuterium, were communicated. In this communication the results of investigations of the reaction mechanism of the reduction of diazonium salts with formaldehyde, the reduction of aldehydes with ethyl alcohol in the presence of aluminum ethylate, and the oxidation of phenylhydrazine with cupric sulfate and potassium ferricyanide will be summarized. The mechanism of these reactions was studied with the aid of the heavy isotope of hydrogen.

Reduction of Diazonium Salts with Formaldehyde*

We saw [1] that in the reduction of diazonium salts with ethyl alcohol and hypophosphorous acid the radicals of the diazonium salts in the process of forming benzene derivatives take up hydrogen from the weaker C—H or P—H covalent bonds but not from the stronger polar O—H bonds of the reducing agent. Analogously (see below) during the oxidation of phenylhydrazine, hydrogen is transferred to the phenyl radical from the N—H but not from O—H bonds.

One might suppose that the reduction of diazonium salts with formaldehyde dissolved in heavy water would lead to the formation of reaction products not containing deuterium, since the radicals of the diazonium salt will take up the less strongly bound hydrogen of the C—H bonds of the formaldehyde and not the deuterium of the O—H bonds of the reaction medium.

Actually, however, we detected that the products formed contain a considerable quantity of deuterium and, consequently, the reduction of diazonium salts with formaldehyde proceeds by a different mechanism than the reduction by alcohol or hypophosphorous acid.

The experiments were conducted in the following manner [3]. Dry diazonium salts obtained in the usual way were dissolved in diluted heavy water cooled to 0°, and 40% formaldehyde (d 1.15) and potassium hydroxide (about 40 ml and 25 g, respectively, per 0.2 mole of diazonium salt) in dilute heavy water were added in drops to the solution. The reaction products were either distilled off from the reaction mixture or extracted from it with ether. After the usual purification and drying the reaction products were fractionated: benzene b.p. 79.5-80°, n_D^{21} 1.5002-1.5012; toluene b.p. 109.5-110.5°, $n_D^{20.5}$ 1.4945-1.4955; anisole b.p. 153-154°, n_D^{21} 1.5170-1.5175,** and burned.

The conditions of the experiments and the results of the analyses of the water from the combustion are set forth in Table 1. In Column 6 of this table are set forth the data concerning the increment in the density of the water in the initial reducing mixture (calculated with an allowance for the dilution with heavy water of the water in the formaldehyde solution). As the reaction proceeded diazonium salt was added to the reducing mixture. The increment in the density of water corresponding to this at the end of the reaction was somewhat different (Column 7). The arithmetic means of the quantities in Columns 6 and 7 are given in Column 8.

The content of deuterium in one particular position of the molecule (Column 9) was determined by multiplying the observed density of the water from its combustion by the total number of hydrogen atoms ($\underline{m}$) in the given compound. As previously [1], we denote the ratio of the quantities set forth in Columns 9 and 8 as the percent transfer of deuterium (Column 10).

It is evident from the data of Table 1 that the percent of transfer of deuterium varies from 19 to 34 during the formation of various hydrocarbons and of anisole. The causes of these variations were not clear to us and will be explained in what follows.

* For a brief note on this see [2].

** For compounds obtained in various experiments.

The presence of deuterium in the compounds being formed indicates that the formaldehyde hydrogen atoms do not transfer directly to the diazonium salt radical. In all probability it was to be assumed that the formaldehyde hydrogen is initially transferred to some intermediate compound formed by the incomplete reduction of the diazonium salt, and adds to this latter at the nitrogen atom. As is well known, hydrogen in N–H bonds is rapidly exchanged with the deuterium of water; therefore, during the further conversions of the indicated intermediate compound it would not be the initial light hydrogen of formaldehyde which would be transferred to the radical of the diazonium salt but the exchanged hydrogen having the same isotopic composition as the hydrogen of the reaction medium. Deuterium, therefore, appears to be present in the compound being formed.

TABLE 1

Reduction of diazonium salts by formaldehyde in alkaline medium

Experiment No.	Quantity and density increment of water for the salt solution		for the reducing mixture		Increment in the density of water (in γ) in the initial reducing mixture	in the mixture at end of the reaction	average	water from the combustion of the hydrocarbons	Percent transfer of deuterium
	(g)	(γ)	(g)	(γ)	calculated			m	
1	2	3	4	5	6	7	8	9	10
Reduction of phenyldiazonium chloride									
1	20	1950	80	1950	1430	1510	1470	370	25
2	60	1130	140	1130	810	860	830	200	24
3	30	1200	75	1200	830	910	870	180	21
4	30	1200	75	1200	830	910	870	160	19
								Average	22
Reduction of p- and o-toluyldiazonium chloride									
p-7	10	0	50	2740	2160	1870	2020	730	36
p-6	10	0	70	2740	2310	2070	2190	670	31
p-9	10	0	70	2740	2310	2070	2190	830	38
p-10	12	0	70	2240	1870	1660	1760	590	34
p-11	10	2740	50	2740	2160	2240	2200	840	38
p-12	12	2740	70	2740	2330	2380	2360	610	26
p-13	30	1130	71	1130	770	850	810	350	43
p-14	20	1490	80	1490	1060	1110	1080	380	36
o-17	20	1490	80	1490	1060	1110	1080	310	29
o-18	20	1200	80	1200	850	910	880	260	30
								Average	34
Reduction of p-anisyldiazonium chloride									
19	22	1200	80	1200	840	900	870	160	18
20	20	1490	80	1490	1050	1110	1080	220	20
								Average	19

It is well known that diazonium salts form hydrocarbons when reduced by arylhydrazines. On the basis of this observation a hypothesis has been advanced to the effect that in every other method of reducing diazonium salts to hydrocarbons, reaction of the unreacted diazonium salts with an intermediately formed arylhydrazine takes place. If this hypothesis were shown to be correct then during the reaction of phenyldiazonium chloride with phenylhydrazine one would expect the formation of hydrocarbons with the same percent transfer of deuterium as during the reduction of phenyldiazonium chloride with formaldehyde. This has not been confirmed experimentally. The percent transfer of deuterium in benzene during the reaction of phenyldiazonium chloride with phenylhydrazine turned out on the average to be equal to 42% in place of 22% during the reduction of phenyldiazonium chloride by formaldehyde.

These experiments were conducted in the following manner. Phenyldiazonium chloride was dissolved in heavy

water and added to a solution of potassium hydroxide also in heavy water. A suspension of phenylhydrazine in heavy water was added to the diazotate solution thus obtained. The mixture was stirred mechanically and cooled with ice. After completion of the reaction benzene was steam distilled off, dried, fractionated (b.p. 79.5-80.0°, n_D^{22} 1.5012). and burned over cupric oxide. The quantity of reagents and the results of the experiments are set forth in Table 2.

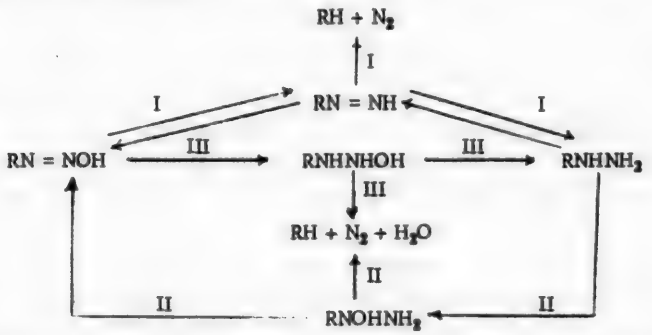
TABLE 2

Reduction of phenyldiazonium chloride by phenylhydrazine in alkaline medium

Expt. No.	Quantity and density increment of water				Increment in the density of water (in γ)				Percent transfer of deuterium
	for the solution of diazonium salt		for the phenylhydrazine solution		in the initial diazotate solution	in the mixture at end of the reaction	average	water from the combustion of the benzene · 6	
	(g)	(γ)	(g)	(γ)	Calculated				
1	40	2530	10	2530	2380	2300	2340	1050	45
2	50	2530	10	2530	2410	2330	2370	920	39
3	103	1040	20	1040	1020	1000	1010	445	44
4	73	1130	30	1130	1090	1070	1080	430	39

The marked difference in the percentages of transfer of deuterium found during the formation of benzene from phenyldiazonium chloride by its reduction with formaldehyde (22%) and phenylhydrazine (42%) compels us to assume that the reduction of the diazonium salt with formaldehyde, in any case for the basic mass of the salt, does not proceed through a stage of intermediate formation of phenylhydrazine.

We consider the following to be the most probable general scheme for reversible oxidation-reduction conversions of diazocompounds and arylhydrazines:*



(Scheme A)

According to this scheme, the intermediate compounds during the reduction of diazonium salts and the oxidation of arylhydrazines should be considered to be α- and β-hydroxyphenylhydrazines and aryldiimines. Depending on the reaction conditions and the oxidation-reduction potentials of the reagents, these intermediate compounds can either undergo further oxidation-reduction conversions without loss of nitrogen, or can be decomposed with evolution of hydrocarbons.

During the oxidation of phenylhydrazine with cupric sulfate in heavy water we observed (see below) the formation of benzene with a percent transfer of deuterium to hydrocarbon close to the percent transfer found during the reduction of phenyldiazoniumchloride by formaldehyde. This supports the hypothesis that both reactions actually proceed through similar intermediate compounds.

The course of the process of reduction of diazonium salts by formaldehyde can presumably be depicted by such a sequence of reactions as the following:

a) addition of two formaldehyde hydrogen atoms to the diazotate (Course III, Scheme A) and

b) mono- or bimolecular decomposition reaction of β-hydroxyphenylhydrazine with evolution of benzene.

* For a similar scheme in less general form see also the earlier [5, 6].

In the course of investigation of the oxidation of phenylhydrazine in acidic and alkaline media (see below) we showed that the phenyl radical forms benzene at the expense of the N–H bonds of compounds present in the system, but not at the expense of their O–H bonds. It can be supposed that an analogous process also takes place in the given case. Stage (b) is assumed just on the basis of analogy with the reactions under consideration.

During the reaction of phenyldiazotate with phenylhydrazine the latter, according to our data, conducts itself just like formaldehyde, reducing the diazotate to phenyldiimine:

$$RNHNH_2 + RN{=}NOH \longrightarrow \underset{\downarrow}{RN{=}NH} + \underset{\downarrow}{RNHNHOH}$$
$$RH + N_2 \qquad RH + N_2 + H_2O$$

Further, both intermediate compounds are decomposed independently of each other.

TABLE 3

Reduction of diazonium salts by formaldehyde in the presence of copper salts

Expt. No.	Quantity and density increment of water for the solution of diazonium salt		Quantity and density increment of water for the reducing mixture		Increment in the density of water (in γ) in the initial reducing mixture	Increment in the density of water (in γ) in the mixture at end of the reaction	Increment in the density of water (in γ) average	Increment in the density of water (in γ) water from the combustion of hydrocarbons and anisole*	Copper salt
	(g)	(γ)	(g)	(γ)					
B-1	34	1010	90	1050	795	845	815	0	$CuSO_4$
B-2	30	1385	70	1385	900	1000	950	2	$CuSO_4$
B-3	50	1495	70	1495	960	1130	1045	9	Cu_2Cl_2
B-4	50	1700	65	1700	1030	1200	1115	0	$CuSO_4$
B-5	50	1700	65	1700	1060	1260	1160	6	Cu_2Cl_2
B-6	50	1700	65	1700	1060	1260	1160	10	Cu_2Cl_2
PT-1	20	1490	80	1490	1060	1130	1100	5	$CuSO_4$
PT-2	25	1130	55	1130	705	830	770	8	$CuSO_4$
PA-1	20	1490	80	1490	1090	1300	1195	3	$CuSO_4$

Phenyldiazotate yields benzene with approximately 20% deuterium, phenylhydrazine (see below) – with approximately 75% deuterium. On the average this should lead to the preparation of benzene containing about 50% deuterium (from the equilibrium concentration of deuterium in the reaction medium), which is close to the quantity found experimentally.

Thus, the reduction of diazonium salts with formaldehyde proceeds with the formation of intermediate compounds, hypothetically oxidized forms of phenylhydrazine, which readily exchange their hydrogen atoms for the deuterium atoms of heavy water. Direct transfer of hydrogen atoms to the diazonium salt radical does not occur.

The routes of hydrogen transfer during this reaction is markedly changed by the addition to the reaction mixture of small quantities of salts of mono- or divalent copper (the latter, in all probability, is reduced by formaldehyde to the monovalent form). The results of the experiments are set forth in Table 3.

It is evident from the data set forth that direct transfer of hydrogen from formaldehyde to the diazonium salt radical takes place in this case.

The mechanism of this catalytic reaction is apparently clearer than that of reactions without catalyst. It can be portrayed by a scheme similar to that of Waters [7] for the Sandmeyer reaction:

$$RN_2^+ + Cu^+ \longrightarrow R\cdot + N_2 + Cu^{++}$$
$$R\cdot + HCHO \longrightarrow RH + \cdot CHO$$
$$\cdot CHO + Cu^{++} \longrightarrow \overset{+}{C}HO + Cu^+$$
$$\overset{+}{C}HO + OD^- \longrightarrow HCOOD$$

* Making allowance for the usual errors of our measurements (5–10 γ, most frequently in the direction of overestimation) these data are evidence of the absence of deuterium in the compounds. The experiments with phenyldiazonium chloride are designated by the letter B, the experiments with p-toluyldiazonium chloride by the letters PT, and the experiments with p-anisyldiazonium chloride by the letters PA.

We think that the division of the process into separate stages with the participation of free radicals is not to be considered obligatory. A very probable variant of this mechanism can be presented in a scheme involving the participation of reaction complexes which do not evolve free radicals in solution.

It was established by special experiments that neither under the reaction conditions nor in considerably more severe conditions (100°, prolonged time) does formaldehyde practically exchange its hydrogen atoms for the deuterium of heavy water.

One would suppose that the influence of copper salts consists in the simple acceleration of the decomposition reaction of the intermediate oxidized forms of phenylhydrazine, so that the latter does not succeed in exchanging its hydrogen atoms with the deuterium of the heavy water and that, consequently, deuterium is not found in the reaction product.

The results of our experiments, communicated below, show, however, that even at 100° the oxidation of phenylhydrazine in heavy water proceeds with the formation of heavy benzene, i.e., that even under these extreme conditions the exchange manages to proceed to a considerable extent.

The results of this portion of the work indicate that the reduction of diazonium salts by formaldehyde proceeds with the intermediate formation of compounds which quickly exchange their hydrogen atoms. In the presence of salts of mono- and divalent copper, however, direct transfer of hydrogen from the C–H bonds of formaldehyde to the hydrocarbon radicals of the diazonium salts proceeds. The indicated change in the mechanism of one particular reaction under the influence of catalyst merits further study. We have demonstrated previously [1] that the reduction reaction of diazonium salts by hypophosphorous acid in the presence of copper salts proceeds at the expense of the hydrogen of the P–H bonds of the latter. We do not have sufficient basis for assuming that this reaction would proceed by another mechanism in the absence of catalyst, i.e., similarly to the reduction reaction with formaldehyde, which is accomplished at the expense of formation of some intermediate compounds. This question must be studied in more detail in the future.

Oxidation of Phenylhydrazine by Cupric Sulfate and Potassium Ferricyanide*

The object of this portion of the investigation was the study of the oxidation of phenylhydrazine into benzene and the elucidation of the source of the hydrogen which enters into the benzene nucleus. In addition, taking into consideration that the oxidation reaction of arylhydrazines and the reduction of diazonium salts can be considered under certain conditions as two coupled reactions of one and the same oxidation-reduction process [5] $RN_2X \xrightarrow{\text{reduction}} RNHNH_2$; $RNHNH_2 \xrightarrow{\text{oxidation}} RN_2X$, we hoped in this way to arrive at the elucidation of the question of the mechanism of the reduction of diazonium salts by formaldehyde.

The formation of hydrocarbons during the reduction of diazocompounds and the oxidation of arylhydrazines can proceed through one and the same or similar intermediate products, as can be seen in the scheme set forth above for the oxidation-reduction conversions of diazocompounds and arylhydrazines (Scheme A).

The oxidation of phenylhydrazine in aqueous solutions by cupric sulfate [9] and by potassium ferricyanide [10] has been experimentally investigated; consequently, in the present work we also employed these oxidizing agents, substituting water containing 1-3% deuterium for ordinary water.

The source of the hydrogen transferred to the phenyl radical of phenylhydrazine in the reaction under investigation can be either water molecules or the hydrazo groups of the phenylhydrazine itself (or intermediate products of its oxidation).

The hydrogen of N–H bonds is ordinarily exchanged very rapidly for the deuterium of heavy water [11, 12], and therefore, the question of a choice between N–H- and O–H-bonds can arise only in the case of commensurability of the rates of the reaction of oxidation of phenylhydrazine and of isotopic exchange. If the rates of both processes are commensurable, then the composition of the reaction products should depend (by analogy with the experiments of reducing diazonium salts with hypophosphorous acid [1]) on whether heavy phenylhydrazine reacts with a solution of oxidizing agent in water of normal isotopic composition or whether light phenylhydrazine reacts with a solution of oxidizing agent in heavy water.

In conformity with this, the phenylhydrazine oxidation experiments were conducted in the following manner.

1. Oxidation by Cupric Sulfate. In the first series (Experiments 1-6, Table 4) a solution of 11 g of phenylhydrazine in 10 ml of acetic acid, diluted with ordinary water, was poured into a boiling solution of cupric sulfate,

* B. E. Gruz participated in this portion of the work; see the preliminary communication [8].

taken in 10% excess, in heavy water. In the second series (Experiments 7-11, Table 4) a solution of 11 g of phenylhydrazine in heavy water and ordinary acetic acid (10 ml) was poured in drops into a solution of $CuSO_4$ in ordinary water. Benzene was distilled off from the reaction mixture as it was formed. After the usual drying and purification the benzene was fractionated (b.p. 79.5-80°, n_D 1.4995-1.5000) and burned. The data are set forth in Table 4.

2. Oxidation by Potassium Ferricyanide was conducted in the cold. Phenylhydrazine in the form of an aqueous suspension was poured into an alkaline solution of the oxidizing agent. Benzene was distilled off from the reaction mixture after the completion of the reaction. The order of addition of reagents and of purification of the benzene obtained was the same as in the cupric sulfate oxidation experiments. The data are set forth in Table 5.

TABLE 4

Oxidation of phenylhydrazine by cupric sulfate in acidic solution

Expt. No.	Quantity of phenylhydrazine (in g)	Quantity of water and its density increment				Increment in the density of water (in γ)				Percent transfer of deuterium
		for the phenylhydrazine solution		for the oxidizing agent solutions		in the initial oxidizing mixture	in the mixture at end of reaction	average	in water from the combustion of the benzene X 6	
		(g)	(γ)	(g)	(γ)	Calculated				
1	11	10	0	80	3060	3060	2610	2840	630	22
2	11	10	0	80	3060	3060	2610	2840	540	19
3	11	10	0	80	3160	3160	2680	2920	640	22
4	11	10	0	80	3160	3160	2680	2920	600	21
5	10	10	0	100	2960	2960	2600	2780	490	18
6	10	10	0	100	2960	2960	2600	2780	550	20
7	11	50	3060	80	0	0	1140	570	240	42
8	11	50	3160	80	0	0	1180	590	210	36
9	11	80	2960	40	0	0	1900	950	440	46
10	10	30	2960	100	0	0	660	330	160	49
11	10	30	2960	100	0	0	660	330	150	45
12	22	35	1530	75	2150	1940	1720	1830	360	20•
13	22	32	1130	60	1130	1020	970	990	280	28••
14	11	60	1450	60	1490	1450	1380	1420	380	27

TABLE 5

Oxidation of phenylhydrazine by potassium ferricyanide in alkaline solution

Expt. No.	Phenylhydrazine (g)	Quantity of water and its density increment				Increment in the density of water (in γ)				Percent transfer of deuterium
		for the phenylhydrazine solution		for the oxidizing agent solutions		in the initial oxidizing mixture•••	in the mixture at end of reaction	average	in water from the combustion of the benzene X 6	
		(g)	(γ)	(g)	(γ)	Calculated				
1	11	40	0	80	3060	2960	1940	2450	1510	61
2	11	30	0	59	3060	2930	1890	2410	1500	62
3	10	70	0	80	2240	2170	1150	1660	1050	63
4	10	70	0	80	2240	2170	1150	1660	1170	70
5	10	70	0	80	2070	2010	1070	1540	1030	67
6	10	70	0	80	2070	2010	1070	1540	1030	67
7	11	80	2960	40	0	0	1880	940	900	96
8	11	80	2830	40	0	0	1800	900	1030	115
9	11	80	2830	40	0	0	1800	900	940	105
10	10	30	2240	120	0	0	440	220	300	136
14	22	20	1010	180	1010	990	960	975	750	77
15	11	70	1030	121	1030	1010	990	1000	720	72
16	11	10	1020	125	1020	990	970	980	720	74

• 40 ml of 96% ethanol was added to the aqueous $CuSO_4$ solution.
•• 50 ml of the absolute ethanol was added to the aqueous $CuSO_4$ solution.
••• Making allowance for exchange with the added potassium hydroxide.

In the last columns of Tables 4 and 5 are set forth values expressing the ratio of the experimentally found content of deuterium in benzene (in one position) to the calculated average of the equilibrium content of deuterium in all the hydrogen atoms of the reaction mixture which are capable of exchanging.

As we have previously demonstrated [1], the magnitudes of the percent of transfer of deuterium obtained in this way characterize the actual ratio of the rates of transfer of deuterium and hydrogen in the reaction under investigation only when the contents of deuterium in the O—H groups of the water and the N—H groups of the phenylhydrazine are identical, i.e., under conditions in which the isotopic exchange does not lead to change in the isotopic composition (Experiment 14, Table 4; Experiments 14-16, Table 5), or proceeds instantaneously.

It is evident from comparison of the data obtained in Experiments 1-6 and 7-11 of Table 4 that the average percent of transfer of deuterium during the oxidation of light phenylhydrazine by cupric sulfate solution amounts to 21%. The percent of transfer is raised to 44% in the oxidation of heavy phenylhydrazine by a solution of the oxidizing agent in ordinary water. The data of experiment 14 show that the percent of transfer of deuterium during the addition of heavy phenylhydrazine to a solution of the oxidizing agent in heavy water amounts to 27%.

The change of the magnitudes of the percent of transfer with changes in the sequence of introduction of heavy water can be explained by the fact that the exchange reaction during the oxidation of phenylhydrazine does not proceed instantaneously, but at a rate commensurable with the rate of the oxidation reaction. During the oxidation of light phenylhydrazine a portion of the benzene is formed from incompletely-exchanged compound. This results in a lower content of deuterium (low percent of transfer) in the hydrocarbon. Exactly as in the oxidation of heavy phenylhydrazine the benzene is partially formed from this latter. This leads to an increased deuterium content in comparison with that calculated (complete exchange prior to the oxidation reaction).

A similar pattern is also observed during the oxidation of phenylhydrazine by potassium ferricyanide in alkaline medium. In this case the percent transfer of deuterium during the addition of light phenylhydrazine to a solution of the oxidizing agent in heavy water (Experiments 1-6, Table 5) is equal to 65, while during the oxidation of heavy phenylhydrazine by a solution of the oxidizing agent in ordinary water (Experiments 7-11, Table 5) it becomes even higher than 100. In the absence of exchange between the phenylhydrazine and the reaction medium (Experiments 14-16, Table 6) the percent transfer of deuterium is on the average equal to 74.

The results obtained are thus evidence of the fact that during the oxidation of phenylhydrazine by cupric sulfate and potassium ferricyanide, benzene is formed at the expense of the hydrogen atoms of the N—H bonds of phenylhydrazine. The picture is strongly obscured by isotopic exchange, but this conclusion can, on the whole, be considered quite well founded.

The results obtained are also of interest since they open up the possibility of evaluating the rates of rapid exchange reactions which cannot successfully be determined by ordinary methods. The separation of exchanging substances ordinarily requires at least several minutes, and, consequently, it is difficult to evaluate correctly the degree of exchange in periods not exceeding 1-2 minutes. In cases similar to that under investigation, one can set up a model of the exchange between substances that are in contact for a matter of seconds.

Using the formula (I) linking the rates of the exchange and oxidation reactions [1], the ratio of these rates can readily be found for the phenylhydrazine oxidation experiments with both cupric sulfate and potassium ferricyanide. The corresponding values of $\underline{n}$ are set forth in Table 6.

The precision of the determinations of the magnitudes of $\underline{n}$ is not great, and we cannot verify that the magnitudes of $\underline{n}$ for differing conditions of the oxidation of phenylhydrazine are actually different from each other. Taking $n = 0.2$, we obtain the result that the rate of the exchange reaction in all the oxidation reactions studied by us is approximately 5 times greater than the rate of the oxidation reaction.

The data obtained by us are thus evidence of the fact that hydrogen is transferred to the phenylhydrazine radical from its N—H bond and not from the hydrogen of water.

The marked difference in the observed percents of transfer of deuterium during the oxidation of phenylhydrazine with cupric sulfate, on the one hand, and with potassium ferricyanide, on the other (27% and 74%) under conditions in which the exchange between the starting material and the reaction medium does not change their isotopic composition, confirms the hypothesis advanced by Kizhner [13] concerning the differing mechanisms of the oxidation of hydrazines when these two oxidizing agents are used.

We assume that the oxidation of phenylhydrazine proceeds according to the following mechanism.

TABLE 6
Oxidation of phenylhydrazine

Experiment No.	Cupric sulfate n	Potassium ferricyanide n
1	0.22	0.20
2	0.42	0.19
3	0.23	0.17
4	0.31	0.05 (?)
5	0.53	0.11
6	0.37	0.11
7	0.16	0.17
8	0.09	0.37
9	0.58 (?)	0.26
10	0.13	0.11
11	0.11	–

In acidic medium cupric sulfate oxidizes phenylhydrazine to α-hydroxyphenylhydrazine (Course II, Scheme A). The introduction of a hydroxyl group in the α-position is in agreement with the known facts of enhanced reactivity of the secondary hydrogen atom in phenylhydrazine (in comparison with the primary), noted by Kizhner [13] and others.

Homolytic decomposition of the oxidized forms of phenylhydrazine subsequently takes place in the reaction complex without evolution of free radicals in the solution. This ensures migration of hydrogen atoms from the N–H bonds to the phenyl radical. An ionic decomposition process would result in migration of the hydrogen from the more polar O–H bonds.

The oxidation of phenylhydrazine not containing deuterium and the decomposition of the corresponding molecules of α-hydroxyphenylhydrazine require less activation energy, and consequently proceed primarily before the cleavage of the heavy compounds. This explains the low percent deuterium transfer to benzene found by us. We found values of the percent transfer of deuterium equal to 20-30, that corresponded to the literature data concerning the ratio of the reaction rates of isotopically different molecules of any given compound equal to 1: 3-1: 5 and were dependent on the difference of the zero energies of ordinary hydrogen and deuterium compounds. The greater portion of the deuterium-containing intermediate products of the oxidation of phenylhydrazine are converted into the resinous products usually formed during the reaction. An analogous phenomenon, i.e., the accumulation of deuterium in the reaction medium, is observed during the oxidation of heavy isopropyl alcohol $(CH_3)_2CDOH$ by chromic acid [14], during the photochlorination of mixtures of $CHCl_3$ and $CDCl_3$ [15] and so forth.

The results of experiments conducted in the presence of ethyl alcohol favor the assumption that homolytic bond cleavage is not accompanied by formation of free radicals during the oxidation of phenylhydrazine by cupric sulfate (as well as during the reduction of diazonium salts by alcohol and formaldehyde, and during the photodecomposition of phenylmercury hydroxide [16] in alcohol solution). The benzene obtained in these experiments was of the same isotopic composition as in the absence of alcohol. If there were free radicals present in the reaction medium, then one could expect the formation of light benzene at the expense of the removal of hydrogen from the radicals of the weak C–H bonds of the alcohol.

Our data on the oxidation of phenylhydrazine by potassium ferricyanide are in agreement with the hypothesis of Kizhner [10, 13] concerning an intermediate formation under these conditions of phenyldiimine which is very unstable and is entirely converted into benzene (Course I, Scheme A).

The fact that only one hydrogen atom can fit into the diimine molecule for each phenyl radical and consequently, that there is no possibility of choice between H and D atoms, i.e., the assumption of its complete conversion into benzene, can explain the high percent transfer of deuterium found by us under these oxidation conditions.

The formation of these or other intermediate compounds during the reversible interconversion of diazo compounds and arylhydrazines (Scheme A) depends on the oxidation-reduction properties of the reaction medium [5]. It is, consequently, not surprising that the oxidation of phenylhydrazine by potassium ferricyanide and the reduction of phenyldiazotate by formaldehyde proceed by different mechanisms, although they both proceed in alkaline solution. As we have already said, in the first case the formation of phenyldiimine is assumed and in the second, the formation of β-hydroxyphenylhydrazine is assumed.

To exclude the possibility of exchange of hydrogen atoms in the phenylhydrazine nucleus at the time of reaction, several experiments were set up involving exchange with phenylhydrazine in heavy water under conditions of acidic and basic catalysis. As is evident from Table 7, exchange of hydrogen atoms in the phenylhydrazine nucleus for deuterium of heavy water is not observed even under comparatively severe conditions. It is of interest to compare the behavior of phenylhydrazine with that of aniline which exchanges its nuclear hydrogen atoms with considerable rapidity during acidic catalysis [11, 12].

Reduction of Aldehydes by Aluminum Alcoholates*

The question of similarity of the mechanisms of the Cannizzaro and Meerwein reactions has been considered a number of times [18, 19]; it is consequently not devoid of interest to elucidate whether or not there is also a

*For a brief communication on this subject, see [17].

TABLE 7

Exchange of Phenylhydrazine with Heavy Water in Acidic and Alkaline Media. A. Exchange in Alkaline Medium, 20°.

Duration of exchange	Quantity of D_2O (in g)	Content of D in the initial D_2O (in γ)	Quantity		Content of D in the water from the combustion of phenylhydrazine		Exchange in the $NHNH_2$-group %
			of alkali (in g)	of phenylhydrazine (in g)	Found	Calculated	
2 min.	5.0160	2960	1.6120	8.0700	730	760	96.0
20 min.	4.9355	2960	1.3330	7.9320	770	770	100.0
48 hours	4.9485	2960	1.3318	8.3318	760	755	100.5
105 hours	4.9990	3460	1.3560	7.1045	890	920	96.7
12 hours*	5.0820	3460	1.5405	8.5920	890	885	100.5*

B. Exchange in Acidic Medium, 20°.

Duration of exchange	Quantity of phenylhydrazine (in g)	Solution of acetic acid in heavy water			Content of D in the water from the combustion of the phenylhydrazine (in γ)		Exchange in the $NHNH_2$-group %
		quantity (in g)	content				
			of D in the hydroxyl group (in γ)	of acetic acid in 1 g of solution	Found	Calculated	
1 min.	7.6420	7.7583	2710	0.372	760	740	103
3 min.	8.8710	7.6220	2535	0.322	730	680	107
20 min.	7.4560	8.0765	2710	0.372	800	760	105
27 hours	8.4100	7.2490	2535	0.322	730	680	107
49 hours	8.4110	7.2940	2535	0.322	700	680	103
67 hours	7.5395	7.7909	2710	0.372	800	750	106

TABLE 8

Reduction of Furfural and Benzaldehyde by Aluminum Ethylate in Heavy Ethyl Alcohol

Experiment No.	Weight (in g)			Duration of the reaction (in hours)	Content of deuterium (in γ)			
	Aldehyde	C_2H_5OD	$(C_2H_5O)_3Al$		in the hydroxyl group of ethanol	in the water from the combustion of alcohols	in the C—H bonds of the alcohols	
							according to the analysis of water	calc.
Fur. 1	9.6	16.0	7.0	168	6600	21	126	4600
Fur. 2**	11.6	32.0	7.0	72	6600	28	168	5500
Fur. 3	17.4	24.0	5.0	210	7100	14	84	5500
Benz. 1	15.7	24.0	7.0	168	6600	11	88	5100
Benz. 2**	15.7	30.0	5.0	72	6600	18	144	5400
Benz. 3	15.7	24.0	6.5	144	7100	11	88	5500

congruence between these reactions in connection with the source of the hydrogen of the new C—H bond which arises during the conversion of an aldehyde molecule into a molecule of the corresponding alcohol.

A determined quantity of aldehyde was added to a solution of aluminum ethylate in ethyl alcohol containing deuterium in the hydroxyl group, and the mixture was mixed and left to stand at room temperature in a closed flask. The solvent was distilled off from the mixture after a few days and the residue was steam distilled. The alcohol formed from the aldehyde was extracted from the distillate with ether and after eliminating the latter, was redistilled with a branched fractionating column. Fractions were collected boiling in the ranges 169-172° for furfuryl, and 202-205° for benzyl alcohol.

*The exchange proceeds at 100°.

Note. In the "calculated" column figures are set forth for the exchange of the three hydrogen atoms of the $NHNH_2$ = group of phenylhydrazine.

**These experiments differ from the others in the fact that the reacting mixtures were boiled for 1 hour with a reflux condenser and after this were left at room temperature for the time indicated in the table.

Fur. = furfuryl alcohol, Benz. = benzyl alcohol.

The alcohols obtained were burned in a stream of air over cupric oxide at 700-800°. The water from the combustion of the alcohols was analyzed for its deuterium content by the flotation method.

Heavy ethyl alcohol was prepared by addition to absolute alcohol of a determined quantity of deuterium oxide. Dehydration of the alcohol was carried on for twenty-four hours with the aid of metallic calcium. A sample of the heavy alcohol was burned over cupric oxide for isotopic analysis.

In the alcohols formed during the reduction of furfural and benzaldehyde, deuterium could be found both in the bonds with carbon and in the hydroxyl group. The presence of the deuterium in the C−H bonds was of interest to us: deuterium was eliminated from the hydroxyl groups of the alcohols by resubjecting them to steam distillation. 10-15 g of alcohol were ordinarily mixed in the distillate with 1000-1500 ml of water. At the same time there could remain, according to calculation, only very little deuterium (5-7 γ) in the hydroxyl groups of the alcohol molecules. The combustion of furfuryl and benzyl alcohols leads to the dilution of the deuterium contained in them by, respectively, 6 and 8 times, which lowers the final correction for the hydroxyl deuterium to a magnitude (1 γ) that is of no importance relative to the accuracy of our measurements (5-10 γ).

Before proceeding to the discussion of the experimental results, it should be emphasized once more that the question of the source of the hydrogen of the hydroxyl groups of furfuryl and benzyl alcohols has not been elucidated by us. Under the experimental arrangement described, its primary source could not in general be established, since the hydroxyl hydrogen atoms of the alcohols being formed are exchanged with those of ethyl alcohol.

A hydrogen atom can migrate to a carbon atom of the aldehydes undergoing reduction either from the carbon atom (I) or from the oxygen atom (II):

$$RCHO + CH_3CH_2OD \xrightarrow{(C_2H_5O)_3Al} RCH_2OD + CH_3CHO, \quad (I)$$

$$RCHO + CH_3CH_2OD \xrightarrow{(C_2H_5O)_3Al} RCHDOH + CH_3CHO. \quad (II)$$

If, in the first case, the process of migration of hydrogen from a carbon atom of one molecule to a carbon atom of another proceeds without participation of solvent (i.e., if the hydrogen migrates directly to the carbon), then there will not be any deuterium in the C−H bonds of the molecules of the furfuryl and benzyl alcohols isolated by us.

On the other hand, if hydrogen atoms of the hydroxyl groups of the reducing agent serve as the source of new C−H bonds, or if the solvent participates in the transfer of hydrogen atoms from a carbon atom of the reducing agent to a carbon atom of the aldehyde (as, for example, during the reduction of diazonium salts by formaldehyde), then deuterium should be contained in the C−H bonds of the newly-formed alcohols.

There should be only as much deuterium in the new C−H bonds during the migration of hydrogen from oxygen as there was in the hydroxyl groups of the heavy ethyl alcohol.

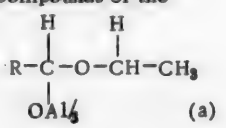
During the carbon-carbon transfer of hydrogen with the participation of solvent, the concentration of deuterium in the C−H bonds should agree with its equilibrium concentration during the complete exchange of all the hydroxyl deuterium atoms and the hydrogen of ethyl alcohol with the migrating hydrogen.

These last quantities are set forth in the column "calculated" of Table 8 in which the results of our experiments are presented.

The data presented in Table 8 leave no doubt that the hydrogen atoms bound to carbon atoms in the reducing agent molecules serve as the source of the hydrogen of the C−H bonds which arise during the reduction of furfural and benzaldehyde, and that the migration of hydrogen from the carbon atoms of one compound to the carbon atoms of another proceeds directly, i.e., without the participation of solvent.

The small increase in the density of the water from the combustion of both alcohols (in comparison with ordinary water) can probably be ascribed to insufficient purification of the water being analyzed, contamination of the alcohols under investigation by deuterium-containing products of side reactions, etc.

The mechanisms proposed up to the present time for the reduction of aldehydes by alcoholates [20] can be roughly divided into two groups. Those mechanisms in which the formation of intermediate compounds of the hemiacetal type (a) is assumed, belong to the first of these groups.



(a)

Those mechanisms which are predicated on the assumption that the reduction process proceeds with the intermediate formation of free radicals [18, 21] can be included in the second group.

The latter assumption has also been discussed in connection with the Cannizzaro reaction.

Kudryavtsev and Shilov [22] recently convincingly demonstrated the catalytic influence of peroxides on the disproportionation of aldehydes.

It is impossible to choose between these mechanisms on the basis of our data since an intramolecular migration of a hydrogen atom from one carbon to another is very probable in the hemiacetal, and this very hydrogen atom would be captured, without participation of the solvent, by radicals during a radical reaction mechanism.

It is important for us that the data obtained are evidence of the participation in the reduction of aldehydes of hydrogen atoms bound to the carbon atoms of the reducing agent and not hydrogen atoms which enter into the composition of the O−H bonds of the compounds present in the system. A similar process of bond homolysis also exists in the Cannizzaro reaction [23].

The authors thank A. I. Brodsky, Member of the Academy of Sciences of the Ukrainian SSR, in whose laboratory these investigations were carried out, for his aid in the work.

SUMMARY

The following conclusions can be drawn on the basis of the results of this and the preceding [1] investigations.

1. During the reduction of diazonium salts and aldehydes by alcohols, hydrogen atoms migrate to the radicals of these compounds from the C−H bonds of the reducing agents.

2. During the reduction of diazonium salts by hypophosphorous acid and the oxidation of phenylhydrazine by cupric sulfate and potassium ferricyanide, the P−H and N−H bonds of the reducing agents serve as the donor of the hydrogen for the compounds being formed.

3. The reduction of diazonium salts with formaldehyde proceeds with the formation of intermediate compounds (probably, oxidized arylhydrazines) which quickly exchange their hydrogen atoms for the deuterium of the water. However, in the presence of catalytic quantities of copper salts the direct migration of hydrogen atoms from the C−H bonds of the reducing agent to the hydrocarbon radicals of the diazo compounds occurs.

4. Several hypotheses concerning the mechanisms of the reactions which were studied and concerning homolytic cleavage processes of bonds in solutions were proposed.

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AMIDATION OF CARBOXYLIC ACIDS WITH AMIDES OF PHOSPHORIC ACID

A. V. Kirsanov and E. A. Abrazhanova

It has recently been shown that during the action of various amides of sulfuric acid on carboxylic acids, the corresponding amides of the carboxylic acids are formed in excellent yields, and the mechanism of these reactions was investigated [1]. It is of interest to establish how the amides of other strong mineral acids will react with carboxylic acids, or, in other words, whether the amidation reaction is a specific reaction of sulfuric acid amides or whether it has a more general character and is characteristic of the amides of all strong mineral acids. The reaction of several phosphoric acid amides with carboxylic acids in pyridine solution has been studied in the present work. The reaction was studied in the case of p-nitrobenzoic acid and the following phosphoric acid amides—the trianilide of phosphoric acid, the tri-p-toluidide of phosphoric acid, the trianilide of phenyl sulfonimidophosphoric acid, the dianilide of phosphoric acid, the dianilide of phenylsulfonamidophosphoric acid, the triamide of phenylsulfonimidophosphoric acid and the monoamide of phenylsulfonamidophosphoric acid [2]. Only the trianilide of phosphoric acid appeared to be an amidating agent; all the other phosphoric acid amides failed to react with carboxylic acids in boiling pyridine solution.

In comparing the amides of phosphoric acid and sulfuric acid as amidating agents, the following can be noted.

1. Carboxylic acids are readily amidated by the saturated anilides of both sulfuric and phosphoric acids.

2. The saturated p-toluidide of phosphoric acid does not amidate carboxylic acids. There are as yet no data concerning the properties of the ditolylsulfamide as an amidating agent.

3. The conduct of the unsaturated amides of sulfuric and phosphoric acids is entirely different: phenylsulfamamic acid is a very energetic phenylamidating agent [1], while the dianilide of phosphoric acid does not react with carboxylic acids. In addition, it is necessary to point out that not one of the amides of arylsulfonimidophosphoric acids is an amidating agent.

After it had been established that the trianilide of phosphoric acid amidates p-nitrobenzoic acid, the action of this anilide on other acids was studied. It was shown that the trianilide of phosphoric acid can be employed for the phenylamidation of both fatty and aromatic acids with the same degree of success as diphenylsulfamide.

The reaction proceeds according to the equation:

$$PO(NHC_6H_5)_3 + RCOOH \longrightarrow RCONHC_6H_5 + HOPO(NHC_6H_5)_2.$$

The following were thus obtained: acetanilide (yield 83.1%), the anilide of propionic acid (78.1%), the anilide of stearic acid (90.6%), phenylacetanilide (88.5%), benzanilide (88.9%), and p-nitrobenzanilide (90.9%).

EXPERIMENTAL

Amidation of p-Nitrobenzoic Acid with Various Amides of Phosphoric Acid

A mixture of 0.002 mole of p-nitrobenzoic acid, 0.002 mole of one of the amides of phosphoric acid (enumerated in the general part) and 5.0 ml of dry pyridine was heated in an oil bath at 125° from 2 to 10 hours. The pyridine was distilled off in a vacuum and the remainder was treated as indicated below. Only in the case of the trianilide of phosphoric acid was p-nitrobenzanilide isolated with a yield of 90.9%; in all the other cases neither the amide nor the phenylamide of p-nitrobenzoic acid could be successfully isolated, while the p-nitrobenzoic acid was almost quantitatively re-isolated (95-98%).

Phenylamidation of Carboxylic Acids by the Action of the Trianilide of Phosphoric Acid

A mixture of 0.002 mole of carboxylic acid, 0.002 mole of the trianilide of phosphoric acid (0.65 g) and 5.0 ml of pyridine was heated with a reflux condenser on an oil bath at 120-125° (all the starting materials must be perfectly dry). After heating for five hours the pyridine was distilled off in a vacuum, 10.0 ml of 2 N soda solution was added to the dry residue, the mixture was carefully stirred, the undissolved portion was separated and the residue was washed with water. The unreacted carboxylic acid could be isolated from the filtrate after acidification. The residue was dried and the anilide of the carboxylic acid was extracted from it with ether (to separate it from the phosphoric acid trianilide which did not enter into the reaction and which is insoluble in ether). The ether was distilled off and the anilide was recrystallized.

Thus, the following were obtained:

Acetanilide with a yield of 0.23 g (83.1%), after recrystallization from water, m.p. 112-113°;

The anilide of propionic acid with a yield of 0.23 g (78.1%), after recrystallization from water, m.p. 103-104°;

The anilide of stearic acid with a yield of 0.65 g (90.6%), after recrystallization from alcohol, m.p. 92-93°;

Phenylacetanilide with a yield of 0.36 g (88.5%), after recrystallization from alcohol, m.p. 116-117°;

Benzanilide with a yield of 0.55 g (88.9%), after recrystallization from alcohol, m.p. 161-162°;

p-Nitrobenzanilide with a yield of 0.55 g, after recrystallization from alcohol, m.p. 208-209°.

All the anilides were identified by the melting point of a mixed sample with the known pure substances.

SUMMARY

1. The reaction of p-nitrobenzoic acid with the trianilide, tri-p-toluidide and dianilide of phosphoric acid and with the trianilide, dianilide, triamide and monoamide of phenylsulfonimidophosphoric acid, was studied.

2. It was shown that only the trianilide of the phosphoric acid amides enumerated above appears to be a phenylamidating agent.

3. It was shown that the trianilide of phosphoric acid can be successfully employed for the direct phenylamidation of carboxylic acids of the fatty and aromatic series.

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TRIBROMOPHOSPHAZOSULFONARYLS

A. V. Kirsanov and Yu. M. Zolotov

It has recently been found that trichlorophosphazosulfonaryls are formed in very excellent yields during the action of phosphorus trichloride on the sodium salts of the chloroamides of arylsulfonic acids [1]. Itwasof interest to investigate how general this reaction is and whether by using it, it is possible to obtain the hitherto unknown tribromophosphazosulfonaryls according to the formula:

$$ArSO_2NNaCl + PBr_3 \longrightarrow NaCl + ArSO_2N{=}PBr_3.$$

The experiments showed that the reaction of phosphorus tribromide with anhydrous sodium salts of chloroamides of arylsulfonic acids proceeds very readily, and tribromophosphazosulfonaryls are formed as the chief products, although not in such high yields as the trichlorophosphazosulfonaryls. If the reaction is conducted without solvent, then the yields do not exceed 50% of the theoretical, but if the reaction is conducted in a solution of carbon tetrachloride, then tribromophosphazosulfonaryls are formed in yields of 70-85% of the theoretical. The preparation of the tribromophosphazosulfonaryls is always accompanied by the formation of side products and the evolution of a small quantity of free bromine.

The tribromophosphazosulfonaryls are crystalline compounds, colorless or slightly colored with a light yellow color, and with a very faint peculiar odor. Tribromophosphazosulfonaryls are rather rapidly decomposed in moist air and readily react with water, amines, phenols and alcohols.

The tribromophosphazosulfonaryls are comparatively low-melting; they begin to soften on heating in a capillary a few degrees below the melting point and melt with decomposition, being converted into a reddish-brown liquid. The tribromophosphazosulfonaryls are readily soluble in acetone and benzene, and are difficultly soluble in ether and carbon tetrachloride.

EXPERIMENTAL

From 100 to 200 ml of dry carbon tetrachloride and 20 ml of a 1-M solution of phosphorus tribromide in carbon tetrachloride (270.7 g/liter) were added to 0.02 mole of carefully dried and powdered sodium salt of the chloroamide of the arylsulfonic acid. The mixture was energetically stirred for 10-15 minutes. At the same time an appreciable evolution of heat proceeded in the mixture, the residue of sodium salt gradually changed its appearance and the liquid became slightly yellowish. To complete the reaction, the mixture was boiled with a reflux condenser on a water bath for an hour. The reaction mixture became reddish-brown, which is to be explained by the evolution of a small quantity of free bromine. The boiling liquid was then quickly filtered, the residue was discarded, and the filtrate was left to crystallize. On cooling, the tribromophosphazosulfonaryls precipitated in the form of well-formed crystals. The product was drawn off, washed with carbon tetrachloride and dried in a vacuum-desiccator over paraffin and sulfuric acid. By evaporating down the mother liquor, some additional quantity of the product could be obtained. To purify the tribromophosphazosulfonaryls, they were recrystallized from carbon tetrachloride. During all the operations the reaction mixture and the solutions as much as possible should be protected from the action of the moisture of the air. To obtain good yields, the sodium salts of the chloroamides of arylsulfonic acids should be carefully dehydrated. According to the literature data, these salts detonate on heating to the melting point (150-200°). Actually, the sodium salts of thechloroamides detonate with remarkable force on drying in a vacuum at even 80°. It is consequently better to dry these salts at room temperature in a vacuum-desiccator initially over sulfuric acid and then over phosphorus pentoxide, to constant weight, which requires about four days.

In this manner the following were obtained:

Tribromophosphazosulfonophenyl, $C_6H_5SO_2N{=}PBr_3$ yield 6.1 g (71.6%), m.p. 94-97° (uncorr.), crystallized from carbon tetrachloride in the form of fine prisms.

0.2798 g substance: 0.3736 g AgBr; 16.2 ml 0.2046 N NaOH. 0.2858 g substance: 0.3768 g AgBr; 16.5 ml 0.2046 N NaOH. Found: % Br 56.82, 56.11; equivalents of acid during hydrolysis 5.04, 5.02. $C_6H_5SO_2NPBr_3$. Calculated: % Br 56.31; equivalents of acid during hydrolysis 5.00.

Tribromophosphazosulfono-o-tolyl, $o\text{-}CH_3C_6H_4SO_2N{=}PBr_3$, yield 7.52 g (85.4%), m.p. 148-151° (uncorr.); softened at 144°, crystallized from carbon tetrachloride in the form of long needles.

0.2875 g substance: 0.3681 g AgBr; 15.8 ml 0.2046 N NaOH. 0.2618 g substance: 0.3345 g AgBr; 14.5 ml 0.2046 N NaOH. Found: % Br 54.48, 54.37; equivalents of acid during hydrolysis 4.94, 4.98. $C_7H_7SO_2NPBr_3$. Calculated: % Br 54.49; equivalents of acid during hydrolysis 5.00.

Tribromophosphazosulfono-p-tolyl, $p\text{-}CH_3C_6H_4SO_2N{=}PBr_3$, yield 6.86 g (79.0%), m.p. 138-141° (uncorr.), softened at 132°, crystallized from carbon tetrachloride in the form of fine prisms.

0.2176 g substance: 0.2814 g AgBr; 12.0 ml 0.2046 N NaOH. 0.3460 g substance: 0.4602 g AgBr; 19.1 ml 0.2046 N NaOH. Found: % Br 55.03, 54.28; equivalents of acid during hydrolysis 4.96, 4.96. $C_7H_7SO_2NPBr_3$. Calculated: % Br 54.49; equivalents of acid during hydrolysis 5.00.

Tribromophosphazosulfono-α-naphthyl, $\alpha\text{-}C_{10}H_7SO_2N{=}PBr_3$, yield 6.78 g (70.5%), m.p. 157-159° (uncorr.), softened at 152°, crystallized from carbon tetrachloride in the form of coarse prisms.

0.3238 g substance: 0.3824 g AgBr; 16.4 ml 0.2046 N NaOH. 0.2526 g substance: 0.3008 g AgBr; 12.9 ml 0.2046 N NaOH. Found: % Br 50.25, 50.67; equivalents of acid during hydrolysis 4.93, 4.97. $C_{10}H_7SO_2NPBr_3$. Calculated: % 50.37; equivalents of acid during hydrolysis 5.00.

Tribromophosphazosulfono-β-naphthyl, $\beta\text{-}C_{10}H_7SO_2N{=}PBr_3$, yield 6.32 g (66.1%), m.p. 150-153° (uncorr.), softened at 146°, crystallized from carbon tetrachloride in the form of fine prisms.

0.2342 g substance: 0.2780 g AgBr; 12.1 ml 0.2046N NaOH. 0.2608 g substance: 0.3082 g AgBr; 13.4 ml 0.2046 N NaOH. Found: % Br 50.51, 50.29; equivalents of acid during hydrolysis 5.03, 5.00. $C_{10}H_7SO_2NPBr_3$. Calculated: % Br 50.37; equivalents of acid during hydrolysis 5.00

SUMMARY

1. It was shown that tribromophosphazosulfonaryls are obtained in excellent yields by the action of the sodium salts of the chloramides of aromatic sulfonic acids on phosphorus tribromide.

2. Tribromophosphazosulfonophenyl, o-tolyl, p-tolyl, α-naphthyl and β-naphthyl were prepared and described.

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THE REACTION OF DIALKYLPHOSPHOROUS ACIDS WITH ALDEHYDES AND KETONES

VI. ESTERS OF α-HYDROXYPROPYLPHOSPHINIC ACID

V. S. Abramov and N. A. Ilyina

We have shown [1] that aldehydes and ketones react with dialkylphosphorous acids and yield addition products at the carbonyl group. The reaction is of interest on account of the fact that the dialkylphosphorous acids along with a few other acids as, for example, hydrocyanic and sulfurous acids, yield stable compounds which are often crystalline substances. In connection with this, the reaction can be considered to be characteristic of the carbonyl group. The addition of dialkylphosphorous acids to the carbonyl group proceeds in the presence of catalysts, which function can be performed by the alcoholates of the alkaline metals. The reaction proceeds rapidly with the evolution of heat, and, as we represented it, the dialkylphosphorous acids react in the enol form. A scheme was proposed to explain the mechanism of the course of the reaction of dialkylphosphorous acids with carbonyl compounds [2].

The completeness of the reaction depends on the radicals of the carbonyl group. The reaction proceeds better and more completely with aldehydes than with ketones, and, moreover, if the entering radicals increase the polarization of the carbonyl groups, then the reaction also proceeds better and more completely. The indicated rules were verified for a whole series of examples.

Investigations of the preparation and study of the properties of esters of α-hydroxypropylphosphinic acids are described in the present article. Esters of α-hydroxypropylphosphinic acid were obtained by the action of propionaldehyde on various dialkylphosphorous acids. Freshly prepared saturated solution of sodium methylate served as the catalyst for the reaction. The duration of the reaction of the dialkylphosphorous acids with propionaldehyde and the physical properties of the esters of α-hydroxypropylphosphinic acids obtained are set forth in the table.

In considering the data of the table it is first of all evident that the increase in the temperature of the reaction mass is the greater the larger the hydrocarbon radical of the dialkylphosphorous acid. In addition, less catalyst (sodium methylate) is required, the larger the hydrocarbon radical of the dialkylphosphorous acid. A manifold influx of catalyst is required to effect the reciprocal reaction of propionaldehyde with dimethylphosphorous acid, and a total of about 1 ml of it was consumed, while the reaction with dibutyl and diisobutylphosphorous acid proceeds with one or two drops of sodium methylate solution.

The course of the reaction controls the completeness in the yield of the ester of α-hydroxypropylphosphinic acid. The yield of esters is increased with increasing size of the hydrocarbon radical of the dialkylphosphorous acid, but it is necessary to keep in sight in this connection that with increasing size of the ester molecule partial decomposition occurs during distillation; for example, during that of the dibutyl ester of α-hydroxypropylphosphinic acid. The decomposition of esters of α-hydroxyalkylphosphinic acids during heating (distillation) was established previously by us [3].

We determined the purity of the product and the completeness of the reaction by measuring the refractive index. The refractive index of the reaction mixture after reaction is the closer to the coefficient of pure ester of α-hydroxypropylphosphinic acid, the larger the hydrocarbon radical of the dialkylphosphorous acid.

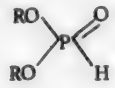
To generalize all that has been said, it can be stated that the reactivity of dialkylphosphorous acids in reactions with carbonyl compounds is the greater, the larger the hydrocarbon radical of the dialkylphosphorous acid.

Such a conclusion contradicts the generally accepted point of view. It is ordinarily considered that substances are the more reactive the smaller the radicals of which they are composed. Such a conclusion (at first glance conflicting) can be explained. According to the investigations of A. E. Arbuzov [4], dialkylphosphorous acids occur

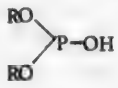
Reaction between Dialkylphosphorous Acids and Propionaldehyde and Constants of the

Dialkylphosphorous acid	Quantity of reacting substances (in g)		Increase in temperature (in °C)	n_D^{20} before distillation	Esters obtained
	Acid	Propionaldehyde			
$(CH_3O)_2POH$	11.0	5.8	23-69	1.4183	$(CH_3O)_2P(O)-CH(OH)-C_2H_5$
$(C_2H_5O)_2POH$	13.8	5.8	24-88	1.4232	$(C_2H_5O)_2P(O)-CH(OH)-C_2H_5$
iso-$(C_3H_7O)_2POH$	12.5	4.5	24-76	1.4180	iso-$(C_3H_7O)_2P(O)-CH(OH)-C_2H_5$
$(C_3H_7O)_2POH$	12.5	4.5	23-106	1.4343	$(C_3H_7O)_2P(O)-CH(OH)-C_2H_5$
$(C_4H_9O)_2POH$	14.4	4.5	25-102	1.4382	$(C_4H_9)_2P(O)-CH(OH)-C_2H_5$
iso-$(C_4H_9O)_2POH$	14.4	4.5	25-122	1.4350	iso-$(C_4H_9O)_2P(O)-CH(OH)-C_2H_5$
$(C_5H_5O)_2POH$	12.2	4.5	24-100	1.4530	$(C_5H_5O)_2P(O)-CH(OH)-C_2H_5$

in two tautomeric forms, in one of which the phosphorus is pentavalent (I) and in the other, travalent (II):



(I)



(II)

It is, however, impossible to separate these two forms due to their tautomeric interconversion. A. E. Arbuzov, M. I. Batuev and V. S. Vinogradova [5] offered a preliminary communication concerning the results of an investigation of the structure of dialkyl phosphorous acids by the method of Raman spectra which demonstrated that a broad, intense line is observed in the dialkylphosphorous acids which corresponds to the valence vibration frequency of P—H. This dialkylphosphorous P—H group is subjected to a strong molecular influence in the form of a hydrogen bond of the P—H. . .P or P—H. . .O type. In addition, the valence vibrations of P=O are observed in the spectra of the dialkylphosphorous acids which also have a diffuse character. Thus, in the liquid state the dialkylphosphorous acids have a pronounced pentavalent phosphonus structure (I). If, in addition to the form (I) there were also the form (II) in the dialkylphosphorous acids, it would lead to the appearance of the frequencies of the O—H group in the Raman spectra of the acids. In the spectra of dipropyl- and dibutylphosphorous acids there is actually detected a narrow band with the O—H valence vibration frequency. The intensity of the O—H band is comparatively small and is masked by intermolecular influences of the hydrogen bond type. Thus, in liquid dialkylphosphorous acids, the form (II) is also present along with form (I) in the propyl and butylphosphorous acids.

As we have already said, the reaction of aldehydes and ketones with dialkylphosphorous acids proceeds in the enol form, i.e., form (II). The greater the possibility of ready formation of form (II), the more readily and intensively the reaction with aldkehydes and ketones should proceed. A similar pattern was also observed by us during the preparation of esters of α-hydroxypropylphosphinic acids; the conclusion which we previously reached, consequently can be formulated as folows: the reactivity of dialkylphosphorous acids with carbonyl compounds is the greater, the greater the possibility of forming their enol forms. Thus, the pattern for the reaction of dialkylphosphorous acids with propionaldehyde which we established is found to be in complete agreement with the investigations of A. E. Arbuzov relative to the structure of dialkylphosphorous acids by the Raman spectra method. The conclusions reached concerning the pattern of the course of the reactions of dialkylphosphorous acids with propionaldehyde were also confirmed for reactions with tetrahydrobenzaldehyde.

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Esters of α-Hydroxypropylphosphinic Acids Obtained

Boiling point (in °)	d_4^{20}	n_D^{20} after distillation	MR_D		Phosphorus content (in %)		Yield of ester (in %)
			calculated	found	calculated	found	
116-117 (1 mm)	1.1834	1.4413	37.17	37.48	18.45	18.70, 18.73	25.83
120-121 (1.5 mm)	1.0955	1.4360	46.40	46.78	15.81	15.88, 15.65	52.5
112-113 (2 mm)	1.0299	1.4295	55.64	56.01	13.83	13.91, 13.65	48.0
126-128 (1 mm)	1.0454	1.4365	55.64	56.08	13.83	13.84, 14.05	30.6
130-132 (1 mm)	1.0241	1.4382	64.88	64.62	12.30	11.75, 12.05	43.4
139-140 (2 mm)	1.0150	1.4378	64.88	65.11	12.30	12.25, 12.46	71.5
129-130 (1 mm)	1.0961	1.4600	54.78	54.98	14.09	13.96, 13.91	49.4

EXPERIMENTAL

Reaction of Dialkylphosphorous Acids with Propionaldehyde

An equimolecular mixture of dialkylphosphorous acid and propionaldehyde was carefully stirred, the temperature measured, and the catalyst – a freshly prepared saturated solution of sodium methylate – added dropwise it; an increase in the temperature was observed. Subsequent portions of sodium methylate were poured in only when the temperature of the mixture began to fall. Introduction of the catalyst was ceased when addition of the next portion did not give an increase in the temperature. Upon completion of the reaction the products were distilled. The course of the reaction and the physical constants of the esters obtained are set forth in the table.

It was ordinarily possible to limit ourselves to one vacuum distillation to obtain analytically pure esters. The methyl, ethyl and allyl esters were exceptions.

SUMMARY

1. The action of dialkylphosphorous acids on propionaldehyde was studied and 7 new esters of α-hydroxypropylphosphinic acids were obtained, the structure and constants of which are set forth in the table.

2. It was established as a result of the investigation that the reaction of dialkylphosphorous acids with carbonyl compounds proceeds the more readily and completely, the larger the hydrocarbon radical of the acid. This conclusion is found to be in full agreement with the conclusions concerning the structure of the dialkylphosphorous acids formed by studying them with the Raman spectra method.

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* See Consultants Bureau Translation, page 709.

PARACHORS OF CERTAIN ESTERS OF ETHYLENEGLYCOLARSENIOUS ACID

Gilm Kamai and K. I. Kuzmin

It has been shown in a number of works which have recently appeared [1, 2], that investigation of the parachors of organic compounds permits certain particulars of the fine structure of organic compounds to be established.

Conclusions concerning one or another particular of the fine structure are made on the basis of comparison of the experimentally found parachors with those calculated from the group values and the corresponding corrections, taking account of the interaction of atoms not directly bound to each other in various structural variations. This method has been successfully applied for the study of the structure of various compounds with long hydrocarbon chains. Up to the present time, little attention has been paid to the study of the structure of cyclic compounds with long side chains.

Gibbling [3] considers that in alkylbenzenes the side chain is deflected in the direction of the aromatic ring under the influence of polar molecules. This requires the introduction of a correction for the deflection for the first three members of the chain, after which the normal magnitude of the standard value of the CH_2 group, equal to 39.8 is reached. The corrections for the deflection of the chain according to the data of Gibbling, amout to:

$$C_6H_5-C-C-C-C-C$$
$$0\ \ -2.4\ -0.6\ -1.3\ \ 0$$

It should be noted, however, that the calculations of Gibbling were based on a very small amount of experimental data and as a consequence of that, are not entirely accurate.

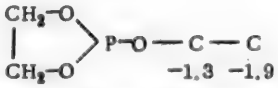
There is information in the literature concerning the parachors of cyclic compounds with longer side chains. We have calculated from the data of Vogel [4] that for the side chains of phenol ethers it is necessary to introduce the following corrections:

$$C_6H_5-O-C-C-C-C-C-C$$
$$-1.7\ -1.3\ -1.8\ -0.3\ -0.3\ -1.4$$

It follows from the parachors of methylcyclohexane [5], octylcyclohexane [6] and octadecylcyclohexane [6] that the average difference of the standard values applying to one CH_2 group of the side chain, ΔCH_2, amounts to: for the range from methylcyclohexane to octylcyclohexane $\Delta CH_2 = 39.4$, and for the range from methylcyclohexane to octadecylcyclohexane $\Delta CH_2 = 39.8$.

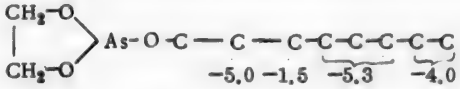
Thus, the corrections for the side chain of cyclic paraffins are considerably less than the corrections for ethers of phenol and alkylbenzenes.

In 1950 B. A. Arbuzov and V. S. Vinogradova [7] initiated a study of the parachors of cyclic esters of inorganic acids. They studied the parachors of the cyclic esters of carbonic, sulfurous and phosphorous acids. B. A. Arbuzov and V. S. Vinogradova employed the following corrections for the interaction of the side ester chain with the ring in the cyclic esters of phosphorous acid:



We have studied the parachors of certain esters of ethyleneglycolarsenious acid.* The data obtained are presented in Table 1.

Corrections for the interaction of the side ester chain with the ring calculated from the data of Table 1, amount to:



* The esters of ethyleneglycolarsenious acid were synthesized by Z. L. Khisamova.

TABLE 1

Ester	Observed parachor	C. E.*	S. V.**
Methyl	254.7	0.7	254.0
Ethyl	289.2	0.8	288.4
Propyl	327.7	1.0	326.7
Hexyl	432.1	1.8	430.3
Octyl	504.3	2.5	501.8

on the average for each group.

The observed magnitudes of the corrections are considerably different from the corresponding corrections for the esters of ethyleneglycolphosphorous acid and phenol ethers. In all probability, the nature of the atoms forming the ring exerts a strong influence on the magnitude of the corrections for the side chain.

The deviation of the standard value for the CH_2 group (from the normal quantity observed even in CH_2 groups very far removed from the ring) in the phenol ethers and in the esters of ethyleneglycolarsenious acid leads us to think that there are apparently some specific structural peculiarities in the molecules of cyclic compounds with a side chain which depend on the presence of the ring. The character of these peculiarities has not been exposed up to the present time.

The study of the parachors of the esters of ethyleneglycolarsenious acid demonstrated that the parachors found experimentally are in excellent agreement with those calculated theoretically, with the application of a twofold correction for parallelism for each CH_2 group, i.e., $-2 \cdot 2.2$. The calculated data are set forth in Table 2.

TABLE 2

Ester	S. V.	C. E.	Parachor		Discrepancy (in %)	Corrections
			calculated	found		
Methyl	254.0	0.7	254.7	254.7	0	—
Ethyl	289.0	0.8	289.8	289.2	+ 0.2	−4.4
Propyl	324.4	1.0	325.4	326.7	−0.4	−8.8
Hexyl	430.6	1.8	432.4	432.1	+ 0.1	−22.0
Octyl	501.4	2.5	503.9	504.3	−0.1	−30.4

What causes the necessity of such a correction has not yet been successfully established. Thus, the question of the structure of the esters of ethyleneglycolarsenious acid can not be considered resolved at the present time. A considerably greater amount of experimental data is required for the conclusive elucidation of the peculiarities of the structure of cyclic compounds with long side chains.

EXPERIMENTAL

Before the determination of the surface tension, the density and the refractive index, all the substances were subjected to vacuum distillation. The surface tension was determined by the maximum bubble pressure method. The surface tension of each substance was measured with two capillary tips at a temperature of $20° \pm 0.1°$. The discrepancy between the results did not exceed 0.2 dynes/cm. The height of the column of manometric liquid was measured with a microcathetometer with an accuracy of up to 0.1 mm. The density of the substances under investigation was measured with an ordinary pycnometer with a volume of about 3 ml with a capillary neck. The refractive indices were determined on an Abbe refractometer. The physical constants of the esters of ethyleneglycolarsenious acid which were investigated are summarized in Table 3.

TABLE 3

Ester	Boiling point (in °)	d_0^{20}	γ_{20}	n_D^{20}
Methyl	51-53 (11 mm)	1.5824	34.8	1.4850
Ethyl	60-62 (11 mm)	1.4723	31.3	1.4788
Propyl	74-75 (12 mm)	1.3949	30.8	1.4760
Hexyl	127.5-129.5 (18 mm)	1.2924	31.3	1.4752
Octyl	123.5-124 (4.5 mm)	1.2389	31.2	1.4748

SUMMARY

1. The parachors of five esters of ethyleneglycolarsenious acid were determined.

2. The problem concerning the structure of the esters of ethyleneglycolarsenious acid and also of other cyclic compounds with long side chains can not be considered solved at the present time.

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* Correction for expansion.

** Standard value.

INVESTIGATIONS IN THE FIELD OF QUINOLINE DERIVATIVES

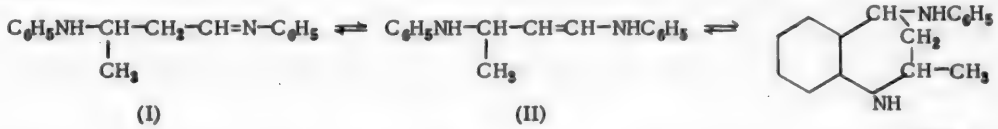
X. SYNTHESES OF QUINOLINES FROM DIETHYLIDENEARYLAMINES

B. I. Ardashev

The mechanism of decomposition of ethylidenarylamine dimers, i.e., the so-called Eibner and Eckstein bases, is directly involved in the formation of quinaldine and its derivatives. Miller considered that it was impossible to obtain more than 22% quinaldine from the dimer of ethylidenaniline [1]. N. S. Kozlov demonstrated in a number of cases that during the formation of quinaldine and its derivatives from aromatic amines and acetylene in neutral medium, dimers of ethylidenarylamines arise [2-6], from which he obtained quinaldine and its derivatives.

To solve the problem of the mechanism of formation of quinolinic bases from diethylidenarylamines it is necessary to know their structure. Eibner considered that the ethylidenaniline dimers were cis and trans isomers of the fumaric and maleic acid type [7]. Later the possibility of tautomerism of bases of the type of the anil of β-anilinobutyraldehyde (I) and diethylidenaniline (II) [8, 9, 10] was demonstrated. In 1951 Zalukaev specified the structure of diethylidenaniline as 2-methyl-4-anilino-1,2,3,4-tetrahydroquinaldine (III) [11, 12].

Thus, the dimers of ethylidenaniline can exist in the form of several tautomers, of which the more stable is the cyclic form:



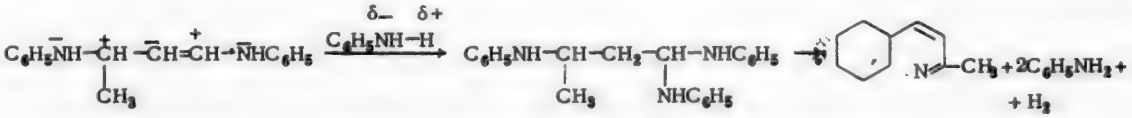
(I) (II) (III)

Upon heating, particularly in acidic medium, the cyclic form is decomposed and is readily converted into quinaldine and aniline with the evolution of hydrogen.

Although the hypothesis has sometimes been expressed that diethylidenarylamines are formed in a Debner-Miller reaction, up to the present time their decomposition has been effected only in a neutral medium or thermally. In spite of this, Zalukaev [11] reported the preparation by him of quinaldine from diethylidenaniline with a yield of 51% of the theoretical; under the conditions of his experiment in neutral medium, however, it was impossible to achieve a yield greater than 25-30%. Correct calculation from his numerical data leads to a magnitude of the yield of 27% [11].

The experiments set up by us for the preparation of quinaldine and its derivatives from the hydrochlorides of diethylidenarylamines lead to a yield of 80-93% of the theoretical.

The catalytic action of aniline hydrochloride was established; it was demonstrated that the maximum yield of quinaldine and its derivatives is obtained with equimolar quantities of the amine salt and the base. In accordance with this, the mechanism of decomposition of the ethylidenaniline dimer in the presence of aniline should be represented in the following manner:



Extreme conditions are not required during the addition of aniline for the decomposition of the base; the reaction can be effected in alcoholic solution with the use of ferric chloride as oxidizing agent. The yield of quinaldine is about 80% of the theoretical. The syntheses from diethylidenarylamines find preparative application for the preparation of several quinolinic bases which are formed in small yields by other methods, for example, 8-toluquinaldine, nitroquinaldines and others. From the corresponding ethylidenaniline dimers 8-toluquinaldine is obtained with a yield of 87%, 6-nitroquinaldine with a yield of 90%.

The investigation conducted has significance for the study of the mechanism of quinaldinic syntheses and, in particular, the mechanism of the Debner-Miller reaction.

EXPERIMENTAL

The dimer of ethylidenaline (trans) was obtained by the method described previously [11]. The yield of the dimer with a m.p. of 117° was 87%.

Synthesis of Quinaldine

Experiment 1. A mixture of 3 ml of concentrated hydrochloric acid and 3 ml of water was poured over 3 g of the dimer base, and 1.5 g of aniline hydrochloride was added and the resulting mixture then heated with a reflux condenser on a boiling water bath for 3 hours. After rendering the solution alkaline with sodium hydroxide, and steam distilling, the quinaldine was precipitated from the distillate in the form of the picrate by a saturated solution of picric acid. The picrate was filtered off, washed with alcohol to remove the excess picric acid and the aniline which partially was adsorbed by the picrate, dried, weighed and the melting point determined. 3.75 g (80%) of quinaldine picrate with a m.p. of 190° was obtained.

No melting point depression was observed in a mixed sample with known quinaldine picrate.

Experiment 2. 1.3 g of aniline hydrochloride and 3.2 g of ferric chloride were added to 2.6 g of the hydrochloride of the dimer base, and 20 ml of alcohol added. The mixture was heated for 3 hours on a boiling water bath with a reflux water condenser and the picrate was isolated as described in the first experiment. 2.2 g (73.3%) of quinaldine picrate with a m.p. of 191° was obtained.

Synthesis of 8-Methylquinaldine

The dimer of ethylidene-o-toluidine (trans) was obtained analogously to the dimer of ethylidenaniline by letting a mixture stand for a week.

The yield of dimer with a m.p. of 115° was 97%.

3 ml of concentrated hydrochloric acid, 2 g of o-toluidine hydrochloride, 4.8 g of ferric chloride were added to 4 g of the dimer base and 20 ml of alcohol was added. From then on the reaction was conducted as in the second experiment. 5 g (86.2%) of the picrate of 8-methylquinaldine with a m.p. of 210° was obtained.

Synthesis of 6-Nitroquinaldine

13.8 g of p-nitroaniline was dissolved in a mixture of 150 ml of alcohol and 100 ml of water to obtain the dimer of 6-nitroethylideneaniline, and 7 ml of freshly prepared acetaldehyde was then added. After heating for 30 mintues with a reflux condenser on a water bath at 70-80°, a precipitate settled out that was initially of an orange color, but which quickly reddened on further heating. The total length of the heating was 1.5 hours, the last 0.5 hour of the heating was carried out on the boiling water bath. The precipitate was filtered off and washed several times with hot water to remove unreacted p-nitroaniline. After drying, 4.5 g of a flocculent powder of a dark brick-red color with a m.p. of 197° was obtained. Since it consisted of a mixture of the cis and trans bases [4], the melting point varied in different experiments within a range of 20°.

The yield amounted to 91.8%, calculated on the basis of the p-nitroaniline taken for the reaction.

10 g of the dimer base was mixed with 5 g of p-nitroaniline, 20 ml of dilute hydrochloric acid (1:1) was added and the mixture was heated with a reflux condenser on a water bath for 3 hours. After cooling the reaction mixture which had been diluted with water, a precipitate settled out, consisting chiefly of p-nitroaniline and an insignificant quantity of admixture of polymerization products. The filtrate was rendered alkaline and 6-nitroquinaldine in a quantity of about 8 g was isolated from it. The 6-nitroquinaldine was recrystallized from hot water; 5.15 g (90%) of product with a m.p. of 170° was obtained. A mixed sample with what was known to be the well-known p-nitroquinaldine did not exhibit any melting point depression.

SUMMARY

1. It was demonstrated that quinaldine and its substituted products in yields of 80-90% are formed from diethylidenarylamines in acidic medium and also in alcoholic solution in the presence of the oxidizing agent ferric chloride.

2. The new method of synthesizing quinolines from diethylidenarylamines can be recommended as a preparative method for obtaining derivatives of quinaldine from o-substituted amines, from nitroamines and for the synthesis of various quinaldine derivatives obtained in poor yields by other methods.

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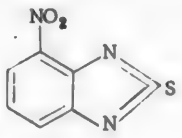
SYNTHESIS OF PIAZOTHIOLE(3,4-BENZO-1,2,5-THIODIAZOLE) AND ITS DERIVATIVES. II.

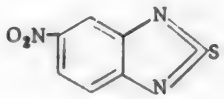
A. M. Khaletsky and V. G. Pesin

In the preceding article [1] we described the synthesis of piazothioleand its nitro-, amino- and acylamino derivatives. In connection with the investigations of Efros and Levit [2], it is of interest to supplement the material of our preceding work with data which we have with respect to the synthesis and investigation of 2-nitro- and 2-amino piazothiole having compared them with the data of the indicated authors

Efros and Levit indicate that during the nitration ofpiazothiolethey obtained 1-nitropiazothiole(I); as regards 2-nitropiazothiole(II), they confirmed that in agreement with the electronic representation developed by them with respect to disturbance of the alignment of the bonds in the benzene ring, the latter (II) can not be obtained by the reaction of 4-nitro-1,2-diaminobenzene with thionyl chloride.

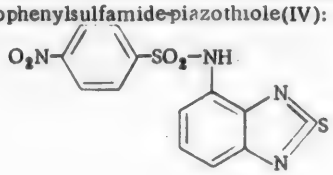


(I)



(II)

We have demonstrated that 2-nitropiazothiole isformed during the reaction of 4-nitro-1,2-diaminobenzene with thionyl chloride, and that 2-nitropiazothiole whenreduced with iron in presence of 1-4% acetic acid is converted into 2-aminopiazothiole. Consequently, the assertion of the authors that 4-nitro-1,2-diaminobenzene does not enter into reaction with thionyl chloride, appears to be erroneous. At the same time it should be noted that it follows from the syntheses of derivatives of aminopiazothiole conducted by us that during the nitration ofpiazothiole the nitro group replaces the hydrogen of the benzene ring in position 1. Thus, during the condensation of aminopiazothiole obtained fromnitropiazothiole(the product of the nitration ofpiazothiole) with the sulfochloride of p-nitrobenzene, p-nitrophenylsulfamidepiazothiole (III) is formed which, upon reduction with sodium sulfide is converted into the corresponding p-aminophenylsulfamide-piazothiole(IV):



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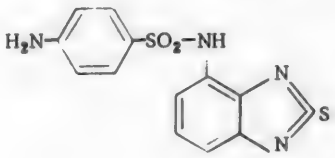
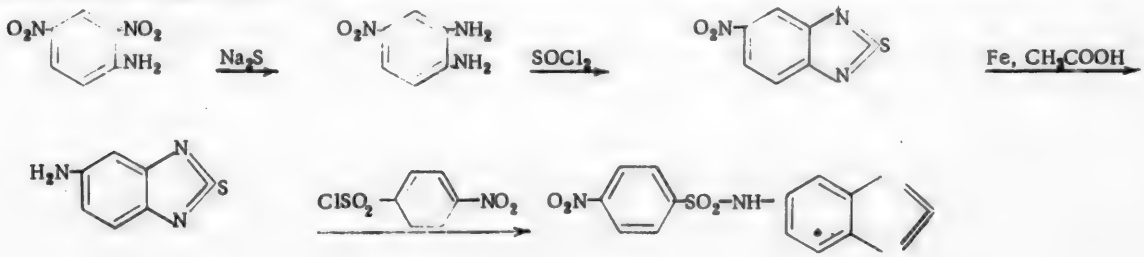
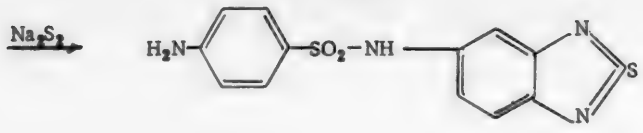


(IV)

The structure of the sulfamides set forth was confirmed by the synthesis of their isomeric compounds on the basis of the following reactions:





It follows from what has been set forth that with respect to the theory of substitutions in the benzene ring, nitro- and aminopiazothioles can exist in the form of two isomers.

EXPERIMENTAL

2-Nitropiazothiole

15.3 g of 1-nitro-3,4-diaminobenzene and 34 g of thionyl chloride (40% excess) were heated with 75 ml of dry toluene while being stirred for 8 hours. The dark colored reaction mixture was cooled and poured into 0.5 kg of a mixture of ice and water. After the liquid layers (toluene and aqueous) had clarified, they were poured into a separatory funnel and the aqueous layer was separated from the toluene layer. The latter along with the crystalline mass was steam distilled. After distilling off the bulk of the toluene together with which an insignificant quantity of 2-nitropiazothiole was extracted, the latter distilled over in the form of almost colorless crystals. 3.3 g (18.2%) of 2-nitropiazothiole with a m.p. of 127-128° was obtained.

2-Nitropiazothiole was slightly soluble in boiling ethyl alcohol, insoluble in methyl alcohol and soluble in acetone and carbon tetrachloride on heating. It crystallized from the latter in the form of colorless clusters.

0.1001 g sub.: 0.1265 g $BaSO_4$. 0.1039 g sub.: 0.1352 g $BaSO_4$. 0.1793 g sub.: 35.53 ml N_2 (17°, 760 mm). 0.1645 g sub.: 33.63 ml N_2 (18°, 756 mm). Found %: S 17.33, 17.87; N 22.95, 23.31. $C_6H_3O_2N_3S$. Calculated %: S 17.68; N 23.20.

2-Aminopiazothiole

A mixture of 6 g of 2-nitropiazothiole, 18 g of iron filings, 100 ml of water and 4 g of acetic acid was heated while being stirred for 0.5 hour to 100°. The cooled mixture was rendered alkaline with sodium carbonate and separated from the iron sludge. The filtrate and the iron sludge were extracted with ether and poured into a crystallizing pan. After driving off the ether 3.1 g of a substance melting at 103-111° was obtained; after recrystallization from hot water, 2.4 g (48%) of crystals with a m.p. of 114° was isolated.

2-Aminopiazothiole dissolves in hot water and many organic solvents; its solubility in hot water is considerably greater than that of 1-aminopiazothiole.

0.0986 g sub.: 0.1552 g $BaSO_4$. 0.1133 g sub.: 0.1726 g $BaSO_4$. 0.1428 g sub.: 34.60 ml N_2 (19°, 756 mm). 0.0908 g sub.: 21.38 ml N_2 (17°, 764 mm). Found %: S 21.64; N 27.34. $C_6H_5N_3S$. Calculated %: S 21.19; N 27.81.

4-Nitrophenyl-1-sulfamide-piazothiole

8.2 g of p-nitrobenzosulfochloride [3] in a mixture with 10 ml of acetone was added gradually to a solution, heated to 50°, of 5 g of 1-aminopiazothiole in 15 ml of pyridine. The mixture was heated 1 hour to 60°, cooled, diluted with water and acidified with hydrochloric acid. The precipitate was filtered off and dissolved in a 4% solution of sodium hydroxide. The filtrate was precipitated with hydrochloric acid, and the precipitate after separation and washing with water was dried at 100°. 8.4 g (75%) of a crystalline substance with a m.p. of 163-164° was obtained.

0.1059 g sub.: 0.1054 g $BaSO_4$. 0.1172 g sub.: 0.1642 g $BaSO_4$. 0.1054 g sub.: 15.35 ml N_2 (21°, 756 ml). 0.1856 g sub.: 27.97 ml N_2 (21°, 756 mm). Found %: S 19.24, 19.45; N 16.19, 16.76. $C_{12}H_8O_4N_6S_2$. Calculated %: S 19.05; N 16.66.

4-Aminophenyl-1-sulfamide-piazothiole

An alkaline solution of 8.4 g of 4-nitrophenyl-1-sulfamidepiazothiole was introduced into a concentrated aqueous solution, heated to 60°, of sodium disulfide and the mixture was heated 1 hour to 65-70°. The filtrate was acidified with hydrochloric acid to a weakly acidic reaction and the yellow-white precipitate was separated and washed with water. The mother liquor was extracted with hot 3% hydrochloric acid, cooled with ice, and the hydrochloride which separated was filtered off. The residue after extraction consisted of a mixture of sulfur with a small quantity of

unreacted nitrocompound. The compounds of the fraction were dissolved in a dilute solution of sodium hydroxide, the solution was treated with animal carbon and the filtrate was again precipitated with hydrochloric acid. The 4-aminophenyl-1-sulfamide-piazothiole which separated out was removed, washed with water and dried at 100°. 5 g (67%) of a crystalline substance with a m.p. of 193-194° was obtained.

0.1118 g sub.: 0.1723 g $BaSO_4$. 0.1068 g sub.: 0.1631 g $BaSO_4$. 0.1531 g sub.: 24.60 ml N_2 (19°, 737 mm). 0.1373 g sub.: 22.36 ml N_2 (20.5°, 737 mm). Found %: S 21.51, 21.15; N 17.81, 17.9. $C_{12}H_{10}O_2N_4S_2$. Calculated %: S 20.91; N 18.30.

4-Nitrophenyl-2-sulfamide piazothiole

The condensation of 2-aminopiazothiole with p-nitrobenzosulfochloride was conducted analogously to its isomer. m.p. 198-200°; yield 77%.

0.1713 g sub.: 0.2473 g $BaSO_4$. 0.1657 g sub.: 0.2278 g $BaSO_4$. 0.1063 g sub.: 16.08 ml N_2 (18°, 732 mm). 0.1253 g sub.: 18.32 ml N_2 (22°, 752.5 mm). Found %: S 19.54, 18.77; N 17.10, 16.74. $C_{12}H_8O_4N_4S_2$. Calculated %: S 19.05; N 16.66.

4-Aminophenyl-2-sulfamide piazothiole

The sulfamide was obtained by reduction of 4-nitrophenyl-2-sulfamide-piazothiole under conditions analogous to the synthesis of its isomer. The extraction of the raw reduction product was conducted with 10% hydrochloric acid; m.p. 245-250°; yield 63%.

0.1281 g sub.: 0.1951 g $BaSO_4$. 0.1133 g sub.: 0.1745 g $BaSO_4$. 0.1608 g sub.: 27.08 ml N_2 (16°, 714 mm). 0.1504 g sub.: 25.0 ml N_2 (16°, 714 mm). Found %: S 21.36, 21.42; N 18.69, 18.54. $C_{12}H_{10}O_2N_4S_2$. Calculated %: S 20.91; N 18.30.

SUMMARY

1. It was found that during the nitration ofpiazothiole the nitro group replaces the hydrogen of the benzene ring in position 1.

2. The following were synthesized: 2-nitro- and 2-aminopiazothiole, 4-nitrophenyl-1-sulfamidepiazothiole, 4-aminophenyl-1-sulfamide piazothiole, 4-nitrophenyl-2-sulfamidepiazothiole and 4-aminophenyl-2-sulfamide-piazothiole.

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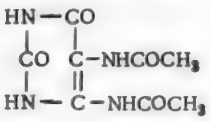
THE CONVERSION OF URIC ACID INTO 8-METHYLXANTHINE

I. STRUCTURE OF THE INTERMEDIATE SUBSTANCE

E. S. Golovchinskaya

The conversion of uric acid into 8-methylxanthine by means of its prolonged heating with acetic anhydride was described for the first time in a patent of the Beringer firm [1] at the beginning of the present century. At that time it was already known that this reaction proceeds in two phases and a hypothesis, concerning the mechanism of the reaction was first proposed [2]. After brief heating of uric acid with acetic anhydride an intermediate substance was successfully isolated which differed from the final 8-methylxanthine in a considerably greater solubility in water. The structure of 4-6-di-(acetylamino)-uracil (I) was then ascribed to it:

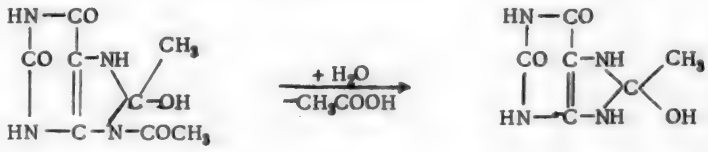


(I)

It was detected that during treatment with alkali only one of its acetyl groups was hydrolyzed. The compound $C_6H_8O_3N_4$ obtained as a result of the hydrolysis was considered as a monoacetyl derivative of 4,5-diaminouracil.

The first detailed investigation of the question of the structure of the intermediate substance was published in 1923 by Biltz and Schmidt [3]. These authors came to the conclusion that the intermediate substance consisted of a bicyclic carbinol (IIa), and not of the 4,5-di-(acetylamino)-uracil (I), as had been previously postulated.

They correspondingly ascribed to that substance obtained from it as a result of the saponification of one acetyl group, the structure (III):



(IIa) (III)

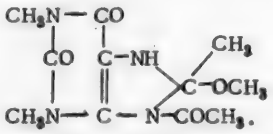
As one of the basic arguments in favor of the carbinol structure of the intermediate substance, Biltz and Schmidt directed their attention to the fact that not only under the action of alkali, but under other saponification conditions as well, the hydrolysis of only one acetyl group occurred. The formation of the closed compound (IIa) was, in their opinion, the result of secondary cyclization, proceeding at the expense of the carbonyl carbon of the second "unsaponified" acetyl group. The only conflict with their assumption concerning a bicyclic structure (IIa) and (III) the authors found in the fact that the characteristic reactions for the hydroxyl group are absent in these substances. They explained this conflict by the position of the hydroxyl group in the molecule and the influence on it of neighboring groupings.

The disputable structure of the intermediate substance has served as the subject of the present investigation. It was begun with the study of its methylation with dimethyl sulfate in an aqueous-alkaline medium. By employing 2 moles of dimethyl sulfate and a pH of 7-8, a crystalline substance (VI) was obtained with a m.p. of 208-209°, which was soluble in alkalis separated from the solutions when they were acidified. According to the analysis it contained two methyl groups which, as was shown by its further conversion into 8-methyltheophylline [4], are bound to the nitrogen of the pyridine portion of the molecule. Its direct yield did not exceed 20%, but a portion of the starting material was recovered from the reaction. By increasing the quantity of dimethylsulfate to 4 moles while maintaining the pH below 8, a reaction mass was obtained which contained no starting material. In this case two substances could be isolated from it: a dimethyl derivative (IV) and a trimethylderivative (Va or Vb). Isolation of the trimethyl derivative and its characterization entailed practically no difficulty, since it is very excellently soluble in

water and considerably less soluble in organic solvents (including chloroform). In order to isolate it from the dimethyl derivative, it was necessary to render the solution obtained after methylation alkaline, and repeatedly to extract it with a large quantity of chloroform. The trimethylderivative crystallized in the form of a crystalline monohydrate with a m.p. of 105-107°. Upon drying it lost 1 mole of water of crystallization and melted at 192-193°. The dimethyl derivative was at once extracted from the acidified solution after completion of the extraction of the trimethylderivative with chloroform. The total yield of substances (IV) and (V) exceeded 80% of the theoretical.

Methylation of 4 moles of dimethylsulfate at a higher pH (8-10) leads to the formation of a mixture of (V) with another substance (VIa). Compound (VIa) crystallized in the form of prisms and melted at 223-224°. According to analysis it consisted of a tetramethyl derivative of the intermediate substance in which all four methyl groups are linked to the nitrogen atoms of the ring; the presence of the methoxy group in it was not detected even in traces. The tetramethyl derivative (VI) can also be obtained from compounds (IV) and (V). By careful methylation of the dimethyl derivative with a stoichiometric quantity of dimethyl sulfate, the formation of the trimethyl derivative proceeds.

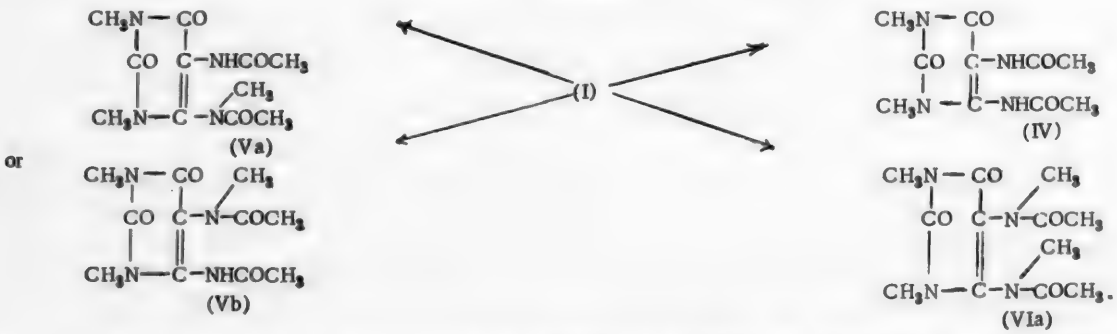
The preparation of a tetramethyl derivative in which all four methyl groups are linked with nitrogen atoms served as the first conclusive refutation of the views of Biltz and Schmidt on the structure of the intermediate substance: if it actually consisted of a bicyclic carbinol, acetylated at one of its nitrogen atoms (IIa), then the replacement of all of its mobile hydrogens with methyl groups should lead to the preparation of compound (VII) containing a methoxy group:



(VII)

The absence of a methoxy group in the tetramethyl derivative seems an argument in favor of the assumption that it consists of 1,3-dimethyl-4,5-di-(acetylmethylamino)-uracil, while the initial, unmethylated intermediate substance would consist of 4,5-di-(acetylamino)-uracil (I) (in agreement with the initial representation of its structure that was rejected after the work of Biltz and Schmidt). In this case the di- and trimethyl derivatives should have the following structures set forth below (Scheme A):

Scheme A



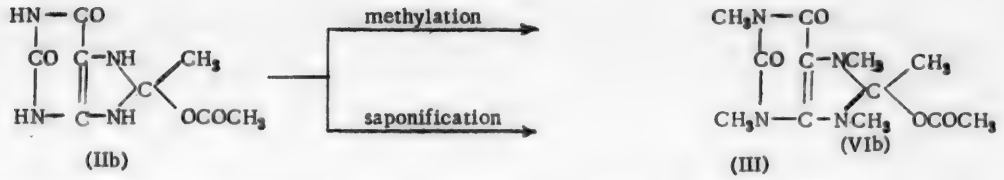
(Va) or (Vb)

(I)

(IV)

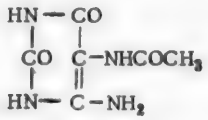
(VIa)

The results obtained on the methylation of the intermediate substance thus demonstrate the incorrectness of the representation of the carbinol structure (IIa). It did not, however, provide a basis for excluding the probability of another cyclic structure in no way previously considered: it could be assumed that it consisted of a carbinol ester in which all four nuclear nitrogen atoms are linked with hydrogen atoms (or with methyl groups), while the acetyl group replaces hydrogen atoms not at the nitrogen, but at the hydroxyl group in position 8, with formation of an ester, but not of an amide bond (IIb). The possibility of such a structure is in complete agreement with the ability of only one acetyl group to undergo hydrolysis and with the absence of the reactions characteristic of the hydroxyl group. In this case thesaponified intermediate substance would consist of a carbinol (III) of precisely that structure which was ascribed to it by Biltz and Schmidt, but the tetramethyl derivative would not contain the methoxy group (VIb):

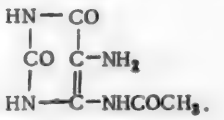


(IIb) (III) (VIb)

If the intermediate substance were 4,5-di-(acetylamino)-uracil (I) (Scheme A), then the substance obtained from it as a result of the saponification of one acetyl group should be one of the two following monoacetyl derivatives (VIII) of 4,5-diaminouracil:



(VIIIa)



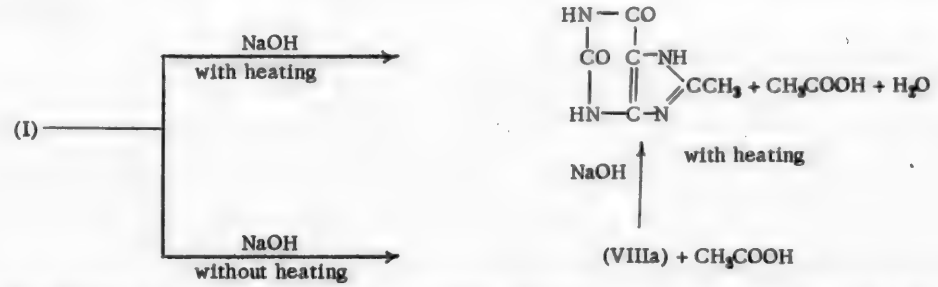
(VIIIb)

The establishment of the true structure of the saponified compound should thus resolve the question of the structure of the initial intermediate substance. The saponified substance was obtained according to the prescription of Biltz and Schmidt, i.e., in a reaction with 10% alkali in the cold. Its monomethyl derivative (IX), described by these same authors and the dimethyl derivative (X) were also obtained. All three compounds failed to react with acetic anhydride in the cold or with acetic acid on heating.

The absence of reaction with acetic acid at once completely excludes the probability of structure (VIIIb), since amino groups bound to a pyrimidine ring in position 5 are always readily alkylated on heating with carboxylic acids [5].

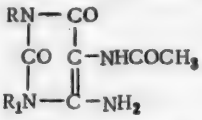
A choice remains between the two possible structures – the closed (III) and the open (VIIIa). In the case of structure (VIIIa) the acetylamino group in position 5, which is not saponified with alkali, should be readily saponified by mineral acid, as this is characteristic of 5-acylamino pyrimidines [6]. This turned out to be the case, as was shown by the results of quantitative determinations of the acetyl group in the substance under investigation and in its two methylated derivatives (IX) and (X). The acetyl groups were subjected to hydrolysis by means of heating with 20% sulfuric acid. One mole of acetic acid was back-titrated in the distillate in all experiments. Saponification of both acetyl groups in the intermediate substance as the result of a sequential two-stage (first alkaline and then acidic) hydrolysis disposed of the basic argument of Biltz in favor of a cyclic carbinol structure for this compound.

On heating the substance under investigation (III or VIIIa) with alkali it is converted into 8-methylxanthine, i.e., conducts itself in a way characteristic of 5-amino-5-acylaminopyrimidines, which in such cases are cyclized with formation of purines. Such a reaction proceeds particularly readily with its mono- and dimethyl derivatives (IX) and (X) which are converted into the 3,8- and 1,3,8-methylxanthines. The intermediate substance can be at once converted into 8-methylxanthine by heating with 10% alkali, i.e., without preliminary saponification in the cold. This reaction with alkali can be expressed by the following scheme (if we start from the fact that it has the open structure (I):



The formation of 8-methylxanthine in this reaction completely explains the failures which have been encountered in the attempts to saponify both acetyl groups in the intermediate substance with alkali and is found in complete agreement with the long established inequality of the amino groups in 4,5-diaminopyrimidines. Only one acetylamino groupis saponified in the cold (in position 4), while the other, more stable, remains untouched. Upon heating, cyclization at the expense of the carbonyl carbon of the second amino group (in position 5) occurs. If the reaction is conducted at once during heating, both processes apparently proceed simultaneously.

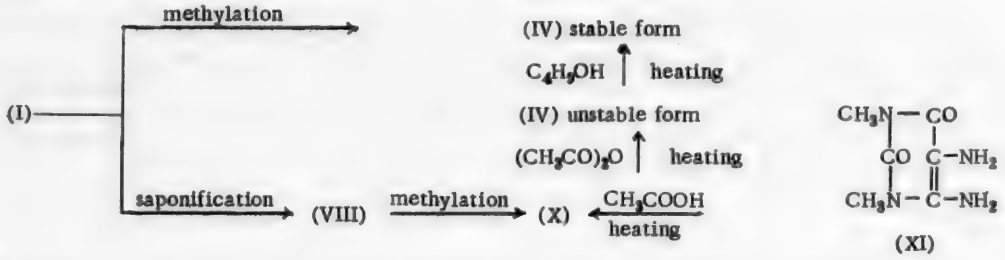
With the object of conclusively verifying the fact that the intermediate substance and its two methylated derivatives, partially saponified with alkali, have the closed structure (VIIIa, IX and X), the synthesis of 3-methyl- and 1,3-dimethyl-4-amino-5-acetylamino-uracils from 3-methyl- and 1,3-dimethyl-4,5-diaminouracils was accomplished.* They were acetylated via heating with glacial acetic acid, i.e., subjected to a reaction widely adopted and repeatedly verified as a method for preparing 4-amino-5-acylamino-uracils. The identity of the compounds obtained in these reactions with the substances (IX and X) was indisputably demonstrated by the fact that the latter, and consequently, the initial nonmethylated substance (VIII) consisted of 4-amino-5-acetylaminouracil:



(VIII): R and R_1 = H;
(IX): R = H; R_1 = CH_3;
(X): R and R_1 = CH_3.

The establishment of their structure once more confirmed that the initial intermediate substance consisted of 4,5-di-(acetylamino)-uracil (I). One of its methylated derivatives (IV) was successfully synthesized from 1,3-dimethyl-4,5-diaminouracil (XI) in a reaction with acetic anhydride. The experiments demonstrated that such a reaction in the cold leads to the formation of a compound monoacetylated in position 5, while after boiling with acetic anhydride in the absence of base for 2 hours, a substance is separated which differs in its properties both from the initial 5-acetylderivative (X) and from the final 8-methyltheophylline formed as a result of the more prolonged reaction. It precipitates from the hot transparent solution in the form of coarse heavy crystals, slightly soluble in organic solvents and entirely unlike the expected substance (IV), which consists of soft, voluminous, cotton-like needles, quite soluble in chloroform in the cold and in the majority of organic solvents on heating. It does not differ from (IV) in melting point (207-209°, since a mixed sample of these two substances displays no melting point depression) or in its capacity to solidify after melting and secondarily melt at 315-325°. It does not differ in its total chemical composition.

Further conversions of the substance obtained showed that it apparently consisted of a dimorphous modification of compound (IV); it was successfully converted to the other form by heating for 2 hours with a large quantity of butyl alcohol (1: 75). During this the substance gradually went into solution and did not crystallize out on cooling. Only after keeping the solution in the cold for many hours did long, fine, soft-as-hair, crystals separate,—all the properties of substance (IV). Evidently, the modification obtained in the reaction with acetic anhydride is unstable on heating with butyl alcohol and is converted under these conditions into the stable form, identical with that obtained earlier as a result of methylation (I).



When the present work had been completed and already prepared for publication, two general articles by Bredereck and his co-workers, devoted to this same question, were published [8].

In a number of cases the authors arrived at results in complete agreement with our results. For example, they consider the mono- and dimethyl derivatives of the intermediate substance after its partial saponification with alkali which they obtained (which they call the monoacetate, in distinction to the initial diacetate) to be 1-methyl- and 1,3-dimethyl-4-amino-5-acetylaminouracils, in complete agreement with the structure (IX and X) established by us and proved by reversible synthesis. They also succeeded in isolating two substances from the methylation of the diacetate with a large excess of dimethylsulfate (6-14 moles).

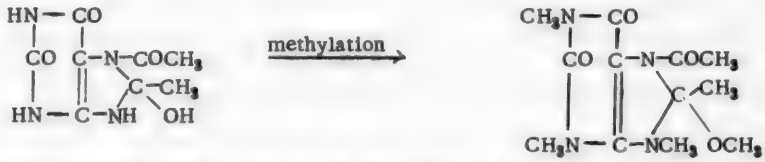
Judging by the described properties and by analysis, these substances (the dimethyl- and tetramethyldiacetates) are doubtless identical with the di- and tetramethyl derivatives (IV) and (VI). The authors state that they did not succeed in obtaining other methylated derivatives of the diacetate. In particular, they did not succeed in preparing the trimethyl derivative (V) described by us apparently, because of the difficulty of isolating and

* 3-Methyl-4,5-diaminouracil was obtained by the reduction of 3-methyl-4-amino-5-isonitrosouracil (an intermediate product in the synthesis of theobromine); 1,3-dimethyl-4,5-diaminouracil was synthesized according to the directions of the Polish chemists Bobranski and Synowiedski [7].

characterizing this very highly water-soluble compound.

It is impossible to agree with the conclusions of these authors with reference to the structure of the intermediate substance (diacetate),* which they consider to be a cyclic carbinol, differing with Biltz only on the question of the location of the acetyl group (at the nitrogen in position 7 and not 9).

Thus, they ascribe the following structure, identical with compound (VI) obtained by us, to the diacetate and its tetramethyl derivative:



At the same time they completely ignore the fact of the absence in the latter of the methoxy group, which completely disproves the probability of the structure set forth by them.

Ignoring the absence of the methoxy group in the tetramethyldiacetate, the authors base the cyclic structure for the diacetate and its methylated derivatives chiefly on the comparison of the properties of the two dimethyldiacetates obtained by them. They consider one dimethyldiacetate to be of an open structure, i.e., 1,3-dimethyl-4,5-di-(acetylamino)-uracil; the other — identical with the compound (IV) described by us — to be the closed form. The authors indicate that the diacetate with an open structure is converted into the closed form by the action of alkali, but do not direct their attention to the contradiction which is involved in their assumption that in the case of the conversion of the open diacetate into the closed form the action of alkali evokes cyclization, while in the case of conversion of the diacetate into the monoacetate it evokes opening of the ring. On the basis of our work it seems much more probable that the dimethyldiacetates obtained by the foreign authors, are not structurally different, but are the two modifications described above of 1,3-methyl-4,5-di-(acetylamino)-uracil (IV), of which one form (obtained in the reaction with acetic anhydride) can be converted into the other by heating with alcohol.

EXPERIMENTAL

1,3-Dimethyl-4-acetylmethylamino-5-acetylaminouracil (V)

8 ml of 32.5% NaOH solution and 8 ml of dimethylsulfate were simultaneously added at an equal rate to a suspension of 5 g of the intermediate substance (I) in 30 ml of water at a temperature of 30-35°. The duration of the addition was 4 hours. The reaction medium was kept alkaline to litmus but neutral to phenolphthalein (pH below 8). The transparent solution was treated with carbon, filtered, rendered alkaline to a pH of 9 and repeatedly extracted with chloroform (the extraction progresses very slowly). The residue after distilling off the chloroform — 4.2 g of slowly congealing oil — was treated with 10 ml of dry acetone. On rubbing with a rod a portion of the substance dissolves, and a portion crystallizes. Dry sulfuric ether (30-40 ml) was poured in and the crystalline mass was drawn off. The weight was 3.64 g, the m.p. 172-174°. It was boiled 3 times with dry benzene and the crystals were drawn off from the hot suspension.

The melting point under these conditions rose to 186-189.5°.

For analysis the substance was dissolved in dry dioxane and ether was added to the solution; m.p. 192-193°. Coarse prisms or elongated plates were obtained. The substance was very excellently soluble in water, soluble in acetone, almost insoluble in benzene, even on boiling, and slightly soluble in sulfuric ether. It was moderately soluble in chloroform, crystallized from alcohol, methylethyl ketone, ethyl acetate and other solvents. When crystallized from solvents containing traces of moisture, it crystallized out with 1 mole of water of crystallization (m. p. 105-107°).

3.600 mg sub.: 5.31 ml 0.01 N H_2SO_4. 3.632 mg sub.: 5.39 ml 0.01 N H_2SO_4. 4.171 mg sub.: 7.511 mg CO_2; 2.178 mg H_2O. 4.712 mg sub.: 8.443 mg CO_2; 2.493 mg H_2O. Found %: N 20.65, 20.74; C 49.14, 48.90; H 5.84, 5.92. $C_{11}H_{16}O_4N_4$. Calculated %: N 20.89; C 49.2; H 6.00.

* The authors consider the true intermediate substance in the reaction of the formation of 8-methylxanthine from uric acid to be not the diacetate but the triacetate. The hydrolysis of the third acetyl group and the formation of the diacetate proceeds, in their opinion, as early as the process of crystallization of the triacetate from water. Since boiling with water apparently should not evoke profound structural changes, this question is not touched upon here; it is not relevant to the elucidation of what structure — closed or cyclic — the intermediate substance has.

Preparation of the Monohydrate. . . 0.95 g of anhydrous substance with a m.p. of 192-193° was crystallized from 10 ml of distilled but not dried methylethyl ketone. 0.6 g of coarse transparent prisms with a m.p. of 105-107° precipitated. An additional 0.25 g with the same melting point precipitated from the filtrate during the addition of ether. It was dried for 24 hours in a vacuum desiccator over H_2SO_4 for analysis.

4.471 mg sub.: 6.27 ml 0.01 N H_2SO_4. 6.167 mg sub.: 8.72 ml 0.01 N H_2SO_4. Found %: N 19.65, 19.79. $C_{11}H_{16}O_4N_4 \cdot H_2O$. Calculated %: N 19.58.

A weighed sample of 0.1018 g of the substance was dried in a vacuum desiccator at 100° over calcium chloride to constant weight. The substance melted and subsequently solidified. The loss in weight was 0.0063 g, which amounted to 6.19%; m.p. 188°; a mixed sample with anhydrous substance melted at 188-192°. The calculated amount of moisture for a compound with 1 mole of water of crystallization was 6.29%.

1,3-Dimethyl-4,5-di-(acetylamino)-uracil (IV)

a) Preparation from 4,5-di-(acetylamino)-uracil (I). The water-alkali solution from the experiment described above which had been extracted with chloroform was acidified to a weakly acidic reaction as indicated by Congo red and extracted a second time with chloroform. The residue after distilling off the chloroform (1.1 g) crystallized from alcohol. Very fine fluffy needles with a m.p. of 206-207.5° were obtained. The melting point of a mixed sample with methylcaffeine was sharply depressed.

The substance was slightly soluble in cold water and quite soluble in hot water, from which it crystallized on cooling. It dissolved in alkaline solutions and precipitated on acidification; it was almost insoluble in benzene, even on boiling, was slightly soluble in hot acetone and in carbon tetrachloride, somwhat more so in ethyl acetate, and was satisfactorily soluble in chloroform. It crystallized in very fine thread-like needles from all the solvents. It crystallized from alcohol 1: 30. It melted at 208-209°. On further heating, it evolved bubbles, subsequently solidified at 225° and again melted at 315-320°.

4.918 mg sub.: 7.65 ml 0.01 N H_2SO_4. 3.118 mg sub.: 4.83 ml 0.01 N H_2SO_4. 2.970 mg sub.: 5.159 mg.: CO_2; 1.607 mg H_2O. 3.723 mg sub.: 6.478 mg CO_2; 1.959 mg H_2O. Found %: N 21.78, 21.70; C 47.38, 47.45; H 6.04, 5.88. $C_{10}H_{14}O_4N_4$ Calculated %: N 22.04; C 47.20; H 5.51.

b) Preparation from 1,3-dimethyl-4-amino-5-acetylaminouracil (X). A mixture of 3 g of 1,3-dimethyl-4-amino-5-acetylaminouracil with 30 ml of freshly distilled acetic anhydride was placed in an oil bath heated to 130°. It was boiled two hours after which the hot transparent solution was poured off from the coarsely crystalline substance into another flask. On cooling this solution, 0.45 g of material crystallized out from it in the form of needles with a m.p. of 315° which was shown to be identical with 8-methyltheophylline. The acetic anhydride was distilled off in a vacuum. The residue – 0.87 g with a m.p. of 180-196° – crystallized from a large quantity of alcohol. Small, heavy, transparent prisms with a m.p. of 207-209° precipitated.

The coarsely crystalline, transparent substance (1.8 g) isolated directly from the reaction melted at the same temperature. It was almost insoluble, even on boiling, in ethyl acetate, benzene, chlorobenzene, methylethyl ketone, very slightly soluble in chloroform and alcohol, somewhat more soluble in water. It reduced an ammoniacal solution of silver oxide.

A mixed specimen with (IV) obtained by method "a" melted at 207-209°.

It was crystallized from 100 ml of butyl alcohol. It all went into solution as a result of prolonged boiling, but on cooling did not precipitate for a long time. After prolonged standing in a condenser, a voluminous precipitate of very soft long needles impregnated with coarse prisms, separated from the transparent solution obtained; these needles were readily soluble in chloroform and other organic solvents and melted at 207°. The mixture of crystals was heated to the boiling point with 30 ml of alcohol, whereupon the needles at once dissolved, while the insignificant precipitate of coarse heavy crystals was left in the flask for a day. Their weight was 0.14 g; their melting point 207-208°. The crystals were cloudy under the microscope; evidently they were in the process of conversion to the needles.

All three substances obtained in reaction "a" and also the prisms from reaction "b" and their mixtures melted at an identical temperature. However, on further heating the melted substance evolved bubbles of gas (224-225°) and solidified. In all cases the solidified substance began to melt at 315-320°. For analysis the substance was crystallized from alcohol and dried in a vacuum desiccator over H_2SO_4.

3.060 mg sub.: 4.78 ml 0.01 N H_2SO_4. 3.689 mg sub.: 5.79 ml 0.01 N H_2SO_4. 3.606 mg sub.: 6.258 mg CO_2; 1.830 mg H_2O. 4.189 mg sub.: 7.240 mg CO_2; 2.183 mg H_2O. Found %: N 21.87, 21.96; C 47.36, 47.17; H 5.68, 5.83. $C_{10}H_{14}O_4N_4$. Calculated %: N 22.04; C 47.20; H 5.51.

1,3-Dimethyl-4,5-di-(acetylmethylamino)-uracil (VIa)

a) Preparation from 4,5-Di-(acetylamino)-uracil (I). 8.5 ml of a 32.5% solution of NaOH and 9 ml of dimethylsulfate were added to a suspension of 5 g of (I) in 30 ml of water at a temperature of 30-35°. It was preliminarily drenched with 3 ml of alkali after which the addition of both reagents was conducted simultaneously at a pH of 9-10. After completion of the reaction the solution treated with carbon and filtered, was alkaline to phenolphthalein and was exhaustively extracted with chloroform. The residue after distilling off the chloroform (4.6 g) was crystallized from 35 ml of alcohol. Elongated flakes crystallized out with a m.p. of 222-224°. The weight was 1.85 g. Ether was added to the alcoholic filtrate. 2.3 g of the monohydrate (V) with m.p. 105-107° was isolated by this means.

Nothing was extracted by repeated chloroform extraction of the aqueous solutions (after acidification). Material with m.p. 222-224° was crystallized from alcohol (1: 16) for analysis. Fine and transparent rectangular plates with m.p. 223-224° were obtained. The material was quite soluble in cold water and the addition of alkali did not increase the solubility. It was slightly soluble in acetone and ethyl acetate in the cold, more soluble on heating, and crystallized in the form of plates. It dissolved in boiling alcohol (6: 100) and was almost insoluble in benzene, even on heating.

1.664 mg substance: 2.40 ml 0.01N H_2SO_4. 1.815 mg substance: 2.63 ml 0.01 N H_2SO_4. 3.830 mg substance: 7.186 mg CO_2; 2.158 mg H_2O. 3.509 mg substance: 6.553 mg CO_2; 1.957 mg H_2O. Found %: N 20.19, 20.28; C 51.17, 50.93; H 6.13, 6.24; OCH_3 and OH (not detected). $C_{12}H_{18}O_4N_4$. Calculated %: N 19.82; C 51.06; H 6.36.

b) Preparation from 1,3-Dimethyl-4-acetylmethylamino-5-acetylaminouracil (Va). 0.25 ml of 32.5% solution of NaOH and 0.25 ml of dimethylsulfate were added alternately, in drops, to a solution of 0.5 g of substance (Va) with m.p. 186-189° in 5 ml of water. The reaction was conducted at pH 9-10 and a temperature of 30-35° for 1.5 hours. The solution which was alkaline to thymolphthalein was extracted with chloroform (the extraction was quickly completed) and the chloroform was distilled off. The crystalline residue with m.p. 205° was crystallized from alcohol. Characteristic transparent plates with m.p. 223-223.5° were obtained. A mixed specimen with the substance obtained as a result of the methylation of 4,5-di-(acetylamino)-uracil at a pH of 8-10 displayed no melting point depression; a mixed specimen with the starting material began to melt at 172°.

c) Preparation from 1,3-Dimethyl-4,5-di-(acetylamino)-uracil (IV). 0.45 ml of a 33% NaOH solution and 0.5 ml of dimethylsulfate were poured simultaneously and dropwise, into a suspension of 0.5 g of substance (IV) in 3 ml of water while the suspension was being stirred. The pH of the solution was about 9 during the reaction. The alkaline solution was extracted with chloroform. The residue after distilling off the chloroform was crystallized from alcohol. The weight was 0.45 g and the m.p. 223-224°. The melting point of a mixed specimen with the preceding was not depressed. Nothing was extracted by chloroform from the extracted solution after its acidification.

1,3-Dimethyl-4-acetylmethylamino-5-acetylaminouracil (V)

Preparation from 1,3-dimethyl-4,5-di-(acetylamino)-uracil (IV). 0.2 ml of a 32.5% alkali solution and 0.2 ml of dimethylsulfate were added alternately, in drops, and during intensive stirring, to a suspension of 0.5 g of substance (IV) (m.p. 206-207°) in 5 ml of water. The duration of the reaction (at pH 8) was 1.5 hours. The alkaline solution was repeatedly extracted with chloroform and the residue after distilling off the chloroform was treated with dry acetone and ether. The substance which crystallized was separated and boiled twice with dry benzene; m.p. 179°. The melting points of mixed samples were as follows: 1,3-dimethyl-4-acetylmethylamino-5-acetylaminouracil with (Va), obtained as a result of the methylation of 4,5-di-(acetylamino)-uracil (I) (m.p. 186-189°) 179-184°; with (VIa) obtained by the same method (m.p. 223-224°) 164-167°; with the starting material (IV) melting began at 166° and melting occurred at 172-174°.

The characteristic transparent prisms of the monohydrate with m.p. 105-107° were obtained after crystallization from moist methylethyl ketone.

The chloroform-extracted solution was acidified and again extracted with chloroform. The residue after distilling off the chloroform was crystallized from alcohol; m.p. 207°. A mixed specimen with the initial material melted at 206-207°.

4-Amino-5-acetylaminouracil (VIII)

30 g of 4,5-di-(acetylamino)-uracil (I) was dissolved in 300 ml of 10% NaOH solution. The solution was shaken with carbon, filtered and left to stand at room temperature for 10 days. It was acidified with 10% H_2SO_4

to a weakly acidic reaction as indicated by Congo red, cooled to complete precipitation of the material, and filtered. Bright yellow elongated plates were obtained. The weight was 16.1 g. The material was crystallized from 900 ml of water. The mother liquor was concentrated in a vacuum and the substance thereby isolated was crystallized again from water. The total yield of recrystallized substance was 12 g.

4.320 mg substance: 6.221 mg CO_2; 1.663 mg H_2O. 3.460 mg substance: 4.984 mg CO_2; 1.270 mg H_2O. Found %: C 39.29, 39.31; H 4.34, 4.10. $C_6H_8O_3N_4$. Calculated %: C 39.13; H 4.34

3-Methyl-4-amino-5-acetylaminouracil (IX)

a) Preparation from 4-Amino-5-acetylaminouracil (VIII). 8 ml of dimethylsulfate was added to a filtered solution of 3.7 g of 4-amino-5-acetylaminouracil in 26 ml of 5.6% KOH solution and the reaction mass was periodically shaken for 1 hour. The formation of fine white needles began after 20 minutes. It was left to stand for 3 hours, after which it was filtered and the residue washed with alcohol and ether. The weight was 2.8 g, the m.p. 276-278°. On standing, 0.24 g more of the same needles separated from the filtrate. The total yield consequently amounted to 1.5 g (65%).

The material was crystallized from 100 ml of aqueous alcohol (1: 1). The twice-crystallized substance melted at 285°. It was dried for 24 hours in a vacuum desiccator for analysis. Fine white needles, soluble in water and insoluble in chloroform, were obtained. The substance dissolved in alkalis and separated from the alkaline solution on acidification. It crystallized from a large quantity of alcohol.

2.190 mg substance: 3.76 ml 0.01 N H_2SO_4. 3.920 mg substance: 6.69 ml 0.01 N H_2SO_4. 3.792 mg substance: 4.945 mg CO_2; 2.027 mg H_2O. 5.229 mg substance: 6.800 mg CO_2; 2.811 mg H_2O. 0.2568 g substance: 0.0376 g H_2O – loss on drying (150°). Found %: N 24.03, 23.90; C 35.58, 35.49; H 5.98, 6.01; H_2O 14.5. $C_7H_{10}O_3N_4 \cdot 2H_2O$. Calculated %: N 23.93; C 35.90; H 6.00; H_2O 15.3.

b) Preparation from 3-Methyl-4,5-diaminouracil. 2 g of 3-methyl-4,5-diaminouracil and 20 ml of glacial acetic acid were boiled for 4 hours with a reflux condenser. After cooling, the crystallized mass was filtered and washed with ether. The weight was 2.42 g, the m.p. 292-293°. A mixed specimen with the material obtained by method "a" had m.p. 292°. It was crystallized from 100 ml of aqueous alcohol (1: 1). 0.4935 g of the substance lost 0.0756 g on drying at 140°, i.e., weight loss on drying 15.3%. An ammoniacal solution of silver oxide was reduced with formation of a mirror.

1,3-Dimethyl-4-amino-5-acetylaminouracil (X)

a) Preparation from 4-amino-5-acetylaminouracil (VIII). 4.1 ml of dimethylsulfate and 3.9 ml of 32.5% NaOH solution were added alternately, in 0.5 ml portions, during stirring, to a suspension of 3 g of 4-amino-5-acetylaminouracil in 10 ml of water. There was an interval between the addition of each portion of alkali of 5 minutes and of 20-25 minutes between the addition of each portion of dimethylsulfate. Everything gradually went into solution and then crystallized in a viscous mass. The reaction mixture was neutralized to a weakly acidic reaction as indicated by Congo red, filtered and the residue washed with ice water. The weight was 1.6 g and the m.p. 268-270° (traces of liquefaction at 262°). A mixed specimen with 3-methyl-4-acetylamino-5-aminouracil (m.p. 285°) melted at 255-262°, i.e., displayed a definite melting point depression. It was twice crystallized from alcohol for the analysis. Fine soft needles or elongated rectangular plates were obtained. An ammoniacal solution of silver oxide was reduced with the formation of a mirror. The material was quite soluble in water, soluble in hot alcohol 1: 60, almost insoluble in xylol, ethyl acetate, chloroform, even on heating. It crystallized in the form of needles from ethyl and butyl alcohols and a large quantity of methylethyl ketone: m.p. 280°.

3.201 mg substance: 5.94 ml 0.01 N H_2SO_4. 3.626 mg substance: 6.75 ml 0.01 N H_2SO_4. 3.085 mg substance: 5.179 mg CO_2; 1.491 mg H_2O. 4.082 mg substance: 6 762 mg CO_2; 2.041 mg H_2O. Found %: N 25.98, 26.07; C 45.54, 45.21; H 5.41, 5.60. $C_8H_{12}O_3N_4$. Calculated %: N 26.41; C 45.28; H 5.66.

b) Preparation from 3-Methyl-4-amino-5-acetylaminouracil (IX). 0.55 ml of dimethylsulfate was added to a solution of 1 g of 3-methyl-4-amino-5-acetylaminouracil in 2.8 ml of 8% NaOH solution. The mixture was shaken for 45 minutes whereupon the mass crystallized. It was filtered and the crystalline substance was washed with alcohol. The weight was 0.8 g and after a single crystallization from alcohol the m.p. was 264-268°. A mixed specimen with the starting material displayed a distinct melting point depression, with the dimethyl derivative obtained by method "a" melted at 264-268° and did not differ from it in other physical properties.

c) Preparation from 1,3-dimethyl-4,5-diaminouracil. 1) 5 g of 1,3-dimethyl-4,5-diaminouracil was boiled for 5 hours with 50 ml of glacial acetic acid. The acetic acid was distilled off from the transparent solution in

a vacuum. The residue was treated with ether and separated. The weight was 5.75 g and the m.p. 265-266°. It was crystallized from alcohol. Fluffy white needles were obtained. There was no melting point depression in mixtures with the substances obtained by methods "a" and "b" and it did not differ from them in its properties. An ammoniacal solution of silver oxide was reduced in the cold with the formation of a mirror. 0.3 g was again crystallized from 20 ml of alcohol for the analysis.

4.290 mg substance: 8.04 ml 0.01 N H_2SO_4. Found %: N 26.28. $C_8H_{12}O_3N_4$. Calculated %: N 26.41.

2) 1 g of 1,3-dimethyl-4,5-diaminouracil was stirred with 10 ml of acetic anhydride; some evolution of heat was observed. The mixture was left to stand for two weeks at room temperature in a flask with a ground stopper. In the course of this period the mass became somewhat more mobile. It was filtered and the white crystals obtained were washed with ether. The weight was 1.02 g and the m.p. 266-270°. Mixed samples with the substances obtained in the preceding (Preparation "c", Experiment 1) and succeeding (Preparation "c", Experiment 3) experiments did not display any melting point depression.

3) 1 g of 1,3-dimethyl-4,5-diaminouracil was stirred with 10 ml of dry pyridine and 5 ml of acetic anhydride. The mixture was left to stand for 2 weeks at room temperature; it crystallized in this period. It was filtered and the crystalline residue was washed with ether. The weight was 1.1 g (92.7%) and the m.p. 271-272°. No melting point depression was detected in mixed specimens with samples of the materials obtained in the preceding experiments.

SUMMARY

The structures of the intermediate substance formed in the transformation reaction of uric acid into 8-methylxanthine and also of the compound obtained from it as a result of the hydrolysis of one acetyl group were studied. A series of methylated derivatives of these two substances was synthesized and described. It was found that all the compounds studied are mono- and diacetylated derivatives of 4,5-diaminouracil and not binuclear carbinols (8-hydroxy-8-methyl-8,9-dihydroxanthines). Some reactions and transformations of these compounds were studied.

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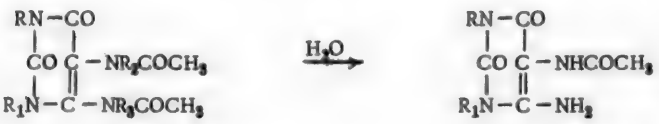
* See Consultants Bureau Translation, page 145.

THE CONVERSION OF URIC ACID INTO 8-METHYLXANTHINE

II. ACTION OF MINERAL ACIDS ON 4,5-DI-(ACETYLAMINO)-URACIL

E. S. Golovchinskaya

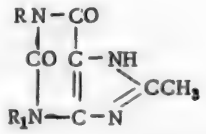
It was shown in the preceding communication [1] that the intermediate substance isolated in the conversion of uric acid into xanthine consists of 4,5-di-(acetylamino)-uracil (I). That paper included a description of the synthesis of three methylated derivatives of this substance (II, III and IV) and also of the mono- and dimethyl derivatives (VI and VII) of 4-amino-5-acetylaminouracil (V), obtained from (I) as a result of the hydrolysis of one acetyl group:



I: R, R_1, R_2 and R_3 = H
II: R and R_1 = CH_3; R_2 and R_3 = H
IIIa: R, R_1 and R_3 = CH_3; R_2 = H
IIIb: R, R_1 or R_2 = CH_3; R_3 = H
IV: R, R_1, R_2 and R_3 = CH_3

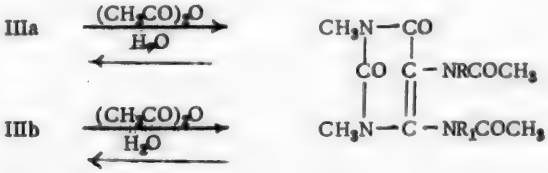
V: R and R_1 = H
VI: R = H; R_1 = CH_3
VII: R and R_1 = CH_3

On heating compound (I) and compound (V) obtained from it as a result of partial saponification with acetic anhydride, 8-methylxanthine (VIII)* is formed; (VI) is converted under these conditions into 3,8-dimethylxanthine (IX) characterized by methylation to 1,3,7,8-tetramethylxanthine while substances (II) and (VII) are converted into 8-methyltheophylline (X):



VIII: R and R_1 = H
IX: R = H; R_1 = CH_3
X: R and R_1 = CH_3

As was to be expected, heating the tetramethylderivative (IV) with acetic anhydride did not lead to cyclization. The starting material was quantitatively recovered from the reaction. The trimethyl derivative (III) was also not cyclized under these same conditions; it was acetylated with the formation of a substance which contained three acetyl groups (XI). A third acetyl group substituted for the unique labile hydrogen in molecule (III), is readily hydrolyzed with the formation of the initial compound, even when merely heated with water.



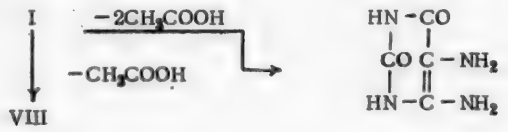
XIa: R = $COCH_3$; R_1 = CH_3
XIb: R = CH_3; R_1 = $COCH_3$

*In this case and in all further work, 8-methylxanthine and its methylated derivatives were characterized by methylation to methylcaffeine.

The experiments involving saponification of (I) and its methylated derivatives by various dilute acids – phosphoric and sulfuric – set up to account for the formation of acetic acid, at once refuted the assertion of Biltz and Schmidt [2] to the effect that the action of mineral acids as well as that of alkalis, leads to the hydrolysis of only one acetyl group. As a matter of fact, the quantity of acetic acid distilled off exceeded 1 mole in all cases. This amount varied from 1.12 to 1.41 moles under various acidic hydrolysis conditions, but did not once reach 2 moles.

Substance	Methods of saponification	Acetyl groups (in %)
(I)	Saponification with 1 N NaOH, acidified with sulfuric acid.	167.4
(I)	Saponification with 1 N NaOH, acidified with phosphoric acid	180.0
(I)	Saponification with phosphoric acid	112.5 Note. The elimination of acetic acid proceeded slowly and was not carried to completion.
(I)	Saponification with sulfuric acid	141.3
(II)	Saponification with sulfuric acid	126.0
(III)	Saponification with sulfuric acid	101.5
Acetylated derivative (III)	Saponification with sulfuric acid	200.9

On the basis of indications in the patent literature [3], the data obtained can be explained by the assumption that during the action of mineral acids on (I) (and also on its derivatives methylated in positions 1 and 3) two parallel processes proceed: a) cyclization into 8-methylxanthine with simultaneous saponification of one acetyl group and b) saponification of both acetyl groups.

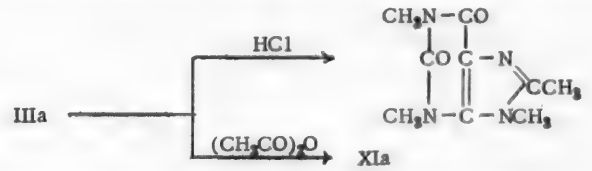


The 4,5-diaminouracil formed in this second process can be subjected to further irreversible conversions (hydrolysis of the amino group in position 4, oxidation and others).

Study of the substances formed as a result of boiling (I) with 10% hydrochloric acid, completely confirmed that, in this case, the saponification reaction is accompanied by cyclization. Comparatively pure, high grade methylxanthine was characterized by methylation to 8-methylcaffeine, was isolated from the reaction mixture. Its yield varied in various experiments, depending on the concentration of hydrochloric acid, approaching 50% of the theoretical in the best case, which was in complete agreement with the data set forth for the quantitative determination of the acetyl groups in compound (I). It appears probable that if both acetyl groups in compound (I) could not be saponified either in acid or in alkaline media by way of cyclization, accompanied in both cases by a saponification process, then the hydrolysis of 1,3-dimethyl-4,5-di-(acetylmethylamino)-uracil (IV) has to proceed otherwise. The possibility of cyclization with evolution of acetic acid molecules is excluded by the absence of free hydrogen atoms in it; it could therefore be expected that the hydrolysis of this compound would lead to the quantitative saponification of both acetyl groups and the formation of 1,3-dimethyl-4,5-di-(aminomethyl)-uracil. Actually, however, attempts to hydrolyze compound (IV) gave unexpected results. Its saponification and, consequently, the elimination of acetic acid proceeded very slowly: after 2 days of heating with acid and distilling off in the form of vapor it was possible to titrate in the distillate in the form of acetic acid only less than 60% of one of the acetyl groups (i.e., about 30% of the total quantity).

The presence of methyl groups bound to the nitrogen atoms of the amino groups apparently stabilizes the bond between these nitrogen atoms and acetyl groups. The same thing was detected in, for example, the trimethyl derivative (III) (see the table). As a result of the acid hydrolysis of this substance, 1 mole of acetic acid was collected in a receiving flask, while with the triacetyl derivative obtained by heating the trimethyl derivative (III) with acetic anhydride, 2 moles were obtained. In this case the acetyl group bound to the methylated amino group is evidently very stable and did not undergo hydrolysis.

The further study of the structure of the substance formed in the reaction of the trimethyl derivative (III) with mineral acid was undertaken with the object of determining the position of the third methyl group in the molecule (III) (structure "a" or "b"). A substance was isolated in excellent yield (77%), from the experiments of heating (III) with 10% hydrochloric acid, which melted at 254° and possessed the physical properties which were described for 8-methylisocaffeine. The analysis and chemical behavior of this substance confirmed that it actually was 1,3,8,9-tetramethylisoxanthine. Its formation was absolute proof of the fact that the trimethylderivative (III) has the structure "a", i.e., consists of 1,3-dimethyl-4-acetylmethylamino-5-acetylaminouracil. In addition, it demonstrated that ring closure by the action of mineral acids, in the absence of cyclization evoked by acetic anhydride, does not require the presence of unsubstituted hydrogen in the acetylated amino group in position 4.



The results obtained permit certain conclusions to be drawn concerning the origin of the carbon in position 8 and the methyl group bound to it in 8-methylxanthines obtained as a result of various cyclization methods. The acetyl group bound to the amino group in position 4 should apparently be considered responsible for the closure of the imidazole ring during the action of mineral acids. Evidence in favor of this includes: a) the formation of 8-methylisocaffeine from the trimethyl derivative (III) in which the acetyl group in position 4 is stabilized by the presence of a methyl group on the same nitrogen atom, while the evolution of acetic acid must consequently occur at the expense of hydrolysis of the acetylamino group in position 5; and b) the quantitative saponification of the acetyl group in position 5 in 4-amino-5-acetylaminouracils on heating with mineral acids [1].

On the other hand, the acetyl group in position 5 indisputably participates in alkaline cyclization. This follows from the conversion of 4-amino-5-acetylaminouracils into methylxanthine by the action of alkali [1] and from the widely used method of preparing purines from 4-amino-5-acylaminopyrimidines.

Insufficient experimental data are available to exclude entirely the possibility of parallel participation of the acetyl group in position 4 in the alkaline cyclization of 4,5-di-(acetylamino)-uracil (I), but the readiness with which this group is saponified by alkali, even in the cold [2], renders this improbable.

A third question: which of the two acetyl groups is responsible for the synthesis of the imidazole ring in the reaction of 4,5-diaminouracils with acetic anhydride, is the subject of further investigation on the part of the author.

EXPERIMENTAL

8-Methylxanthine (VIII)

a) Preparation from 4,5-Di-(acetylamino)-uracil (I) via Heating with Mineral Acids. 2 g of 4,5-di-(acetylamino)-uracil and 10 ml of 10% HCl were boiled on iron gauze with a reflux condenser for 30 minutes. The reaction mixture at once foamed up, the substance quickly went into solution and the solution rapidly became cherry-red and then (after 10-15 minutes) straw-yellow. After cooling, crystals precipitated which were separated and washed with alcohol. The weight was 1 g and the content of methylxanthine according to analysis was 75.3%. Ammoniacal solution of silver oxide was reduced with formation of a mirror.

0.25 g of the substance was dissolved in 4 ml of 6% NaOH solution and methylated with 0.57 ml of dimethylsulfate. The solution crystallized only by the introduction of a seed crystal of methylcaffeine. The crystals were separated and washed with ice water. The weight was 0.1 g and the m.p. 207-208°. A mixed specimen with methylcaffeine did not display any depression of the melting point.

0.5 g of the substance was boiled with 20 ml of water, drawn off while hot, and this operation was again repeated. The weight of the residue was 0.3 g (41.1%) and the methylxanthine content according to analysis was 99.4%. An ammoniacal solution of silver oxide was not reduced. 0.3 g of the washed-off substance obtained was methylated in 3.2 ml of 6% NaOH by the addition of 0.5 ml of dimethylsulfate. The solution formed a uniform crystalline mass even in the process of adding the dimethylsulfate. The melting point of the methylcaffeine obtained was 209-210°. A mixed specimen with methylcaffeine melted at 207-208°.

b) Preparation via Heating with Alkali. 2.25 g of 4,5-di-(acetylamino)-uracil and 4 ml of 10% NaOH solution were heated while being stirred on a boiling water bath for 2 hours. The reaction mass, viscous at the beginning, became liquid and acquired a reddish coloration. The reaction mixture crystallized on cooling. The

substance which separated was transferred to a solution by addition of water and 20% NaOH solution. The turbid reddish solution which was obtained was filtered and acidified with 18% HCl. The yellow precipitate which thereupon separated out was separated and washed with water. The weight was 1.22 g. The residue was boiled with 40 ml of water and drawn off while hot. The weight was 0.74 g (46%); the content of methylxanthine according to analysis was 94.4%.

The substance obtained did not reduce an ammoniacal solution of silver oxide and did not evolve bubbles on heating with dilute nitric acid.

0.4 g was dissolved in 4.5 ml of 8% NaOH solution and methylated at 25-30° with 0.9 ml of dimethyl sulfate. An abundant evolution of methylcaffeine crystals was observed even during the process of methylation. The weight was 0.3 g and the melting point of the substance which had been washed with cold water was 202-205°. A mixed specimen with methylcaffeine melted at 204-207° (it came loose from the walls of the capillary at 202°). It crystallized from water in the form of completely pure crystals with the characteristics of methylcaffeine.

3,8-Dimethylxanthine (IX)

Preparation from 3-Methyl-4-amino-5-acetylaminouracil (VI). 2 g of 3-methyl-4-amino-5-acetylaminouracil and 4 ml of 10% NaOH solution were stirred on a boiling water bath for 2 hours. After cooling, 10% NaOH solution was added until the substance was entirely dissolved and the solution obtained was filtered and acidified with 18% HCl. The weight of the substance which thereupon separated, crystallizing in the form of fine needles, was 1.7 g; it did not melt on heating to 310°, but reduced ammoniacal solution of silver oxide (evidently, the substance obtained contained some admixture of the starting open acetylamino derivative). It crystallized from water in the form of needles.

1 g of the substance was boiled twice with 50 ml of alcohol; 0.2 g of material with m.p. 290-291° did not dissolve (the starting material). 0.6 g of white needles precipitated from alcohol on cooling. An ammoniacal solution of silver oxide was reduced very slowly.

0.5 g of the substance obtained was dissolved in 4.5 ml of 8% NaOH solution. The solution was methylated with 1 ml of dimethylsulfate. The entire mass crystallized even during the addition of dimethylsulfate (with the pH of the solution above 9). The melting point of the washed substance obtained was 207-208°. A mixed specimen with methylcaffeine melted at the same temperature.

8-Methyltheophylline (X)

a) Preparation from 1,3-Dimethyl-4,5-di-(acetylamino)-uracil (II). 0.5 g of 1,3-dimethyl-4,5-di-(acetylamino)-uracil and 10 ml of freshly prepared acetic anhydride were boiled for 30 hours. The substance went into solution at 120°. The crystals which precipitated on cooling were separated and washed with alcohol and ether. They consisted of needles with m.p. 315-320° and a weight of 0.15 g. The acetic anhydride was distilled off from the filtrate in a vacuum. The residue was washed with cold water and then crystallized from 10 ml of water with carbon; a portion of the substance (a water-insoluble brown resin) remained on the filter. 0.15 g of white needles with m.p. 317-322° precipitated from the filtrate. A mixed specimen of both substances melted at 315-322°. The substance was crystallized twice from distilled water for analysis.

3.701 mg substance: 7.57 ml 0.01 N H_2SO_4. 3.761 mg substance: 7.63 ml 0.01 N H_2SO_4. Found %: N 28.63, 28.37. $C_8H_{10}O_2N_4$. Calculated %: N 28.86. Presence of OCH_3 not detected.

b) Preparation from 1,3-Dimethyl Uric Acid*. 0.5 g of 1,3-dimethyl uric acid, 5 ml of acetic anhydride and several drops of dimethylaniline were boiled on an oil bath for 80 hours. The transparent solution obtained evolved crystals on cooling to 0° which were drawn off and washed with ether. 0.3 g of white needles with m.p. 315-320° was obtained. The acetic anhydride was distilled off in a vacuum. The residue (0.15 g) was treated with ether and crystallized from 3 ml of water with carbon. White needles with m.p. 318-318.5° were obtained. A mixed sample of both substances with the substance obtained by method "a" melted at the same temperature.

c) Preparation from 1,3-Dimethyl-4-amino-5-acetylaminouracil (VII). 2.1 g of 1,3-dimethyl-4-amino-5-acetylaminouracil and 4 ml of 10% NaOH solution were stirred and heated on a water bath. The reaction mass became viscous, but dissolved as the heating was intensified. The reaction medium was alkaline to thymolphthalein. After 20 minutes of heating the transparent solution foamed and began to crystallize rapidly. The reaction was continued

* 1,3-Dimethyl uric acid was prepared by a method analogous to that described for the synthesis of unmethylated uric acid [4], i.e., via fusion of 1,3-dimethyl-4,5-diaminouracil with urea. Dimethyldiaminouracil was synthesized according to the directions of Bobranski and Synowiedski [5].

on a boiling water bath for 25 minutes more and then the solidifying mass was dissolved in hot water, filtered and the filtrate was acidified. 1.05 g of fine needles of a bright yellow substance with m.p. 315-316° thereupon separated out. A mixed specimen with 8-methyltheophylline obtained by methods "a" and "b" melted at 315-320°.

0.5 g of the substance was dissolved while being heated in 1.14 ml of 8% NaOH solution and 1.5 ml of water was added, and, in drops, during vigorous stirring, 0.25 ml of dimethylsulfate. The transparent solution gradually crystallized; pH 8-9. On heating on a water bath it all dissolved and crystallized again on cooling. The weight of the filtered and ice water-washed precipitate was 0.44 g and its m.p. 207-208°. The melting point of a mixed specimen with methylcaffeine was 207-208°.

1,3-Dimethyl-4-acetylmethylamino-5-diacetylaminouracil (XI)

1 g of 1,3-dimethyl-4-acetylmethylamino-5-acetylaminouracil (with m.p. 185°) and 20 ml of acetic anhydride were boiled for 40 hours. The material entirely dissolved. The acetic anhydride was distilled off in a vacuum, and the residue was stirred with ether and was drawn off. The weight was 1.16 g and the m.p. 175°. It was boiled with 20 ml of dry benzene. The substance dissolved and on cooling crystallized out in coarse elongated plates, intergrown with each other, with m.p. 179-181°. The melting point of a mixed specimen with the starting material was 157-167°, with methyl caffeine (m.p. 207-208°) was 166-178°.

The substance was dissolved in hot water (1:6) and crystallized on cooling in the form of coarse polyhedral prisms. It crystallized from ethyl acetate as well as from benzene in the form of elongated transparent plates. It did not dissolve in a solution of alkali.

3.185 mg substance: 4.14 ml 0.01 N H_2SO_4. 4.251 mg substance: 5.51 ml 0.01 N H_2SO_4. 3.844 mg substance: 7.109 mg CO_2; 1.868 mg H_2O. 4.133 mg substance: 7.649 mg CO_2; 1.997 mg H_2O. Found %: N 18.20, 18.16; C 50.47, 50.50; H 5.42, 5.40. $C_{13}H_{18}O_5N_4$. Calculated %: N 18.06; C 50.32; H 5.8.

1,3,8,9-Tetramethylisoxanthine

3 g of 1,3-dimethyl-4-acetylmethylamino-5-acetylaminouracil (III) was boiled for 3 hours with 15 ml of 10% HCl, the last 20 minutes with carbon. It was filtered with water and the mixture of acids (acetic and hydrochloric) was distilled off in a vacuum. The dry residue was dissolved in a small quantity of water and neutralized with 10% NaOH solution. An abundant crystalline sediment precipitated. The weight was 1.84 g and the m.p. 252-254°. It crystallized from water (12:100) in the form of fine needles, and from alcohol in the form of elongated plates. It was slightly soluble in boiling benzene, somewhat more soluble in ethyl acetate; it was moderately soluble in cold chloroform and more soluble on heating. M.p. 254°.

4.184 mg substance: 8.06 ml 0.01 N H_2SO_4. 3.621 mg substance: 6.89 ml 0.01 N H_2SO_4. 4.207 mg substance: 7.941 mg CO_2; 2.232 mg H_2O. 3.594 mg substance: 6.820 mg CO_2; 1.920 mg H_2O. Found %: N 26.97, 26.63; C 51.51, 51.79; H 5.94, 5.98. $C_9H_{12}O_2N_4$. Calculated %: N 26.92; C 51.92; H 5.77

SUMMARY

1. As a result of heating 4,5-di-(acetylamino)-uracil with dilute mineral acids, cyclization with formation of 8-methylxanthine proceeds along with hydrolysis of both acetyl groups.

2. Substitution of methyl groups for the mobile hydrogen atoms of the acetylamino group in 4,5-di-(acetylamino)-uracil stabilizes the bond of the acetyl groups with the nitrogen atom and thereby impedes their hydrolytic cleavage.

3. It was established that the trimethyl derivative of 4,5-di-(acetylamino)-uracil, obtained as a result of its methylation with dimethylsulfate, consists of 1,3-dimethyl-4-acetylmethylamino-5-acetylaminouracil. Heating it with dilute hydrochloric acid leads to the formation of 1,3,8,9-tetramethylisoxanthine (8-methylisocaffeine).

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* See Consultants Bureau Translation, page 135.

SYNTHESIS OF DERIVATIVES OF PHENOTHIAZINE-1-CARBOXYLIC ACID

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The object of the present work was the synthesis of the amide and hydrazide of phenothiazine-1-carboxylic acid and a series of their derivatives for the study of their antibacterial action.

It is well known that phenothiazine has a distinct antituberculosis action in vitro [1]. It was of interest to examine how the introduction of such groups as the carbohydrazide and carbamide groups, the presence of which in compounds of the pyridine [2], pyrazine [3] and thiazole [4] series is associated with considerable antituberculosis activity, influenced the activity.

Although phenothiazine-1-carboxylic acid has been described in the literature in sufficient detail [5], the derivatives of interest to us had not been known and it turned out that certain difficulties were involved in their preparation. The formation of the amide of phenothiazine-1-carboxylic acid from its methyl ether did not proceed with aqueous ammonia either in the cold or during heating, and proceeded with alcoholic ammonia in an autoclave with only very small yields. A completely satisfactory yield of the amide was obtained by the reaction of the acid chloride of phenothiazine-1-carboxylic acid with gaseous ammonia. It turned out during the attempts to prepare the acid chloride of phenothiazine-1-carboxylic acid that during the action of excess thionyl-chloride and also during the action of a mixture of phosphoryl chloride and phosphorous pentachloride on the acid, there occurs not only formation of the acid chloride, but also substitution of the chlorine atom for three hydrogen atoms in the phenothiazine molecule. Under these circumstances the acid chloride of trichlorophenothiazine-1-carboxylic acid was obtained, from which the corresponding amide and diethylamide were obtained. The S-dioxide was prepared from the amide.

Boiling phenothiazine-1-carboxylic acid with phosphorous trichloride in benzene also failed to lead to the formation of the acid chloride of this acid, and it was only on heating it in a tube with excess phosphorous trichloride for 20 hours at 95° that the acid chloride was obtained in a yield of 75%. The preparation of the acid chloride by the action of phosphorous pentachloride in benzene on the acid at room temperature proved to be a more convenient method; in this case the reaction was completed in 10 minutes.

The p-anisidide, diethylamide and butylamide of phenothiazine-1-carboxylic acid were prepared by the action of the amines on a benzene solution of the acid chloride. The diethylamide and butylamide consisted of viscous non-crystalline substances. They were converted into the S-dioxides by boiling with hydrogen peroxide in glacial acetic acid.

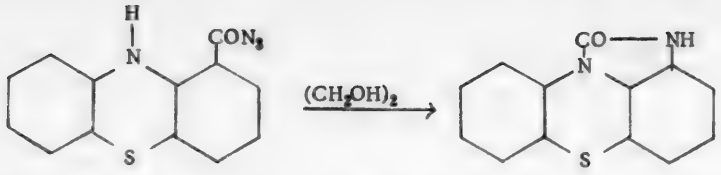
The synthesis of the hydrazide of phenothiazine-1-carboxylic acid was accomplished by boiling its amide with excess hydrazine hydrate for 20 hours.

By heating the hydrazide in alcoholic solution with, respectively, benzaldehyde, p-acetaminobenzaldehyde and p-hydroxybenzaldehyde, the corresponding hydrazones were obtained.

We attempted to utilize the Schmidt reaction to obtain 1-aminophenothiazine. We took chloroform as the solvent while 94 and 98% sulfuric acid was the catalyst; the temperature was varied within the range 30-50° and the quantity of sodium azide was varied from 1 to 1.5 moles, but a highly resinified phenothiazine-1-carboxylic acid was recovered in all cases.

The reaction of the hydrazide of phenothiazine-1-carboxylic acid with nitrous acid was also conducted. By boiling the azide obtained in absolute alcohol a difficultly-soluble, dark red substance was isolated which did not yield to purification and which was not converted into the amine either on boiling with concentrated hydrochloric acid or with alkali.

We succeeded in obtaining the azide of phenothiazine-1-carboxylic acid by the reaction of the acid chloride of the acid with sodium azide, and attempted to subject the acid to a Curtius rearrangement in an ethylene glycol medium with the object of converting it into an amine. However, a urethane was not obtained as a result of this reaction; rather, cyclization with formation of an imidazole ring proceeded:



A similar conversion has been described by Rodionov and Bezinger [6] for azides of N-benzoylated β-amino acids which, instead of the expected isocyanates very readily yield imidazole derivatives on simple heating in anhydrous solvents. Analyses of the substance and its properties – stability on heating with alkali, with concentrated hydrochloric acid and in a mixture with glacial acetic acid – confirmed the imidazole structure of the compound obtained.

All the substances synthesized were investigated with reference to their antituberculosis activity.

The investigation demonstrated that not one of these substances possessed significant antituberculosis activity.

EXPERIMENTAL

Amide of Phenothiazine-1-carboxylic Acid

12 g of phosphorus pentachloride was added to a suspension of 10 g of phenothiazine-1-carboxylic acid in 400 ml of benzene and the mixture was stirred energetically at room temperature for 10 minutes. Almost all the acid went into solution, and the solution acquired a dark red color. Gaseous ammonia was passed into the solution until complete decolorization resulted, and 200 ml of water was then added; after some shaking the benzene layer was separated. The residue, after the benzene had been distilled off, was combined with the material obtained by filtering the aqueous layer and recrystallized twice from benzene. 5 g of the amide with a m.p. of 164-165.5° was obtained. It was a yellow crystalline powder, quite soluble in ether, dioxane, benzene, alcohol, ethyl acetate, and insoluble in water and petroleum ether.

4.431 mg substance: 0.466 ml N_2 (23.5°, 729 mm). Found % N 11.59. $C_{13}H_{10}ON_2S$. Calculated % N 11.57.

S-Dioxide of the Amide of Phenothiazine-1-carboxylic Acid

A mixture of 2 g of the amide of phenothiazine-1 carboxylic acid, 3 ml of a 27% aqueous solution of hydrogen peroxide and 30 ml of glacial acetic acid was heated to boiling for 5 hours. The reaction mass was then poured into 100 ml of cold water. An oily liquid then began to form and quickly crystallized into a light brown powder with a m.p. of 246-255°. The weight was 1.8 g. It recrystallized from alcohol as a white crystalline powder (needles) with a m.p. of 256-258°, quite soluble in alcohol, acetone, and insoluble in benzene, chloroform, ether and water.

3.940 mg substance: 8.201 mg CO_2; 1.304 mg H_2O. 7.438 mg substance: 5.26 ml 0.01 N H_2SO_4. Found %: C 56.80; H 3.70; N 9.90. $C_{13}H_{10}O_3N_2S$. Calculated %: C 56.93; H 3.65; N 10.22.

S-Dioxide of the Butylamide of Phenothiazine-1-carboxylic Acid

7 g of butylamine was added to a benzene solution of the acid chloride of phenothiazine-1-carboxylic acid obtained from 2.5 g of phenothiazine-1-carboxylic acid, 3 g of phosphorus pentachloride and 100 ml of benzene, and the mixture was left overnight. The reaction mass was then diluted with 75 ml of water and the benzene layer was separated while the water layer was extracted with benzene. After distilling off the benzene, 30 ml of glacial acetic acid and 6 ml of a 27% aqueous solution of hydrogen peroxide were added to the residue and the mixture was heated to boiling for 6 hours, after which the reaction mass was poured out into water and the S-dioxide of the butylamide of phenothiazine-1-carboxylic acid (3.1 g, m.p. 126-140°) which was formed was separated and recrystallized twice from benzene. The m.p. was 133.5-135°. It consisted of a white crystalline powder (needles), soluble in alcohol, acetone, chloroform, benzene and insoluble in water and petroleum ether.

3.451 mg substance: 7.752 mg CO_2; 1.650 mg H_2O. Found %: C 61.30; H 5.35. $C_{17}H_{18}O_3N_2S$. Calculated %: C 61.79; H 5.49.

S-Dioxide of the Diethylamide of Phenothiazine-1-carboxylic Acid

15 g of diethylamine was added to the benzene solution of the acid chloride of phenothiazine-1-carboxylic acid obtained from 5 g of phenothiazine-1-carboxylic acid, 6 g of phosphorus pentachloride and 200 ml of benzene, and the mixture was left overnight. The reaction mass was then diluted with 100 ml of water, acidified with hydro-

chloric acid and the benzene layer was separated while the aqueous layer was extracted once more with benzene. After elimination of the benzene the residue was vacuum distilled. A fraction with a b.p. of 220-225° at 0.75 mm was collected which consisted of a viscous, ductile mass. We dissolved this mass in 50 ml of glacial acetic acid and heated it to boiling for 6 hours with 10 ml of a 27% aqueous solution of hydrogen peroxide. On cooling, the S-dioxide of the diethylamide of phenothiazine-1-carboxylic acid with a m.p. of 170-174° was isolated; after recrystallization from alcohol, it had a m.p. of 175-178°. It was a white crystalline powder, quite soluble in alcohol, benzene, chloroform and insoluble in ether.

3.411 mg substance: 7.702 mg CO_2; 1.627 mg H_2O. Found %: C 61.62; H 5.34. $C_{17}H_{18}O_3N_2S$. Calculated %: C 61.79; H 5.45.

p-Anisidide of Phenothiazine-1-carboxylic Acid

1.5 g of p-anisidine was added to a benzene solution of phenothiazine-1-carboxylic acid, prepared from 1 g of phenothiazine-1-carboxylic acid, 1.2 g of phosphorus pentachloride and 40 ml of benzene. Vigorous evolution of heat thereupon occurred, the color of the solution changed, and a yellow-green precipitate began to settle out which was separated and washed with water. After washing the benzene layer with water and eliminating the benzene, a yellow-green residue was also obtained which was added to the other precipitate. The yield was 1.3 g and the m.p. was 208-211°. It melted at 210-212° after recrystallization from isopropyl alcohol. It was a yellow-green crystalline powder, quite soluble in alcohol, acetone, benzene and insoluble in ether and water.

3.910 g substance: 9.871 mg CO_2; 1.508 mg H_2O. Found %: C 68.90; H 4.32. $C_{20}H_{16}O_2N_2S$. Calculated %: C 68.93; H 4.59.

Hydrazide of Phenothiazine-1-carboxylic Acid

A mixture of 3.9 g of the amide of phenothiazine-1-carboxylic acid and 5 g of hydrazine hydrate was heated to boiling for 20 hours, after which the solid mass was recrystallized from alcohol. 3.2 g of the hydrazide with a m. p. of 143-145° was obtained. After recrystallization from benzene the m.p. was 145.5-147°. It consisted of yellow-green needles, quite soluble in alcohol, ether, benzene, acetone, dichloroethane and insoluble in petroleum ether and water.

2.380 mg substance: 0.340 ml N_2 (19°, 738 mm). Found %: N 16.21. $C_{13}H_{11}ON_3S$. Calculated %: N 16.34.

N^2-Benzalhydrazide of Phenothiazine-1-carboxylic Acid

A solution of 1.3 g of the hydrazide of phenothiazine-1-carboxylic acid in 7 ml of alcohol was heated to boiling for 20 minutes with 1 g of benzaldehyde.

After cooling the solution, an orange crystalline powder was isolated which melted at 221-223° after recrystallization from alcohol.

3.700 mg substance: 9.390 mg CO_2; 1.430 mg H_2O. Found %: C 69.26; H 4.32. $C_{20}H_{15}ON_3S$. Calculated %: C 69.54; H 4.35.

N^2-p-Acetaminobenzalhydrazide of Phenothiazine-1-carboxylic Acid

1.5 g of p-acetaminobenzaldehyde in 5 ml of alcohol was added to 1.5 g of the hydrazide of phenothiazine-1-carboxylic acid in 10 ml of alcohol, and the mixture was heated to boiling for 20 minutes. The orange precipitate (weight 2.1 g, m.p. 254-262°) which crystallized after cooling was separated and recrystallized twice from glacial acetic acid; m.p. 264-266°. The substance was difficultly soluble in the ordinary organic solvents.

3.426 mg substance: 8.227 mg CO_2; 1.407 mg H_2O. Found %: C 65.53; H 4.60. $C_{22}H_{18}O_2N_4S$. Calculated %: C 65.67; H 4.47.

N^2-p-Hydroxybenzalhydrazide of Phenothiazine-1-carboxylic Acid

A mixture consisting of 1.5 g of the hydrazide of phenothiazine-1-carboxylic acid and 1 g of p-hydroxybenzaldehyde in 15 ml of alcohol was heated to boiling for 40 minutes and left overnight. 2.15 g of substance with a m.p. of 219-225° was obtained after filtration which, after two recrystallizations from aqueous alcohol, had a m.p. of 242-244°. It consisted of an orange powder, quite soluble in alcohol, acetone, ethyl acetate and insoluble in petroleum ether and water.

4.780 mg substance: 11.649 mg CO_2; 1.810 mg H_2O. 5.930 mg substance: 0.620 ml N_2 (23°, 726 mm). Found %: C 66.50; H 4.23; N 11.52 $C_{20}H_{16}O_2N_2S$. Calculated % C 66.46; H 4.15; N 11.63.

Acid Chloride of Trichlorophenothiazine-1-carboxylic Acid

A mixture consisting of 1.8 g of phenothiazine-1-carboxylic acid and 10 ml of thionyl chloride was heated to boiling for 3 hours. Excess thionyl chloride was distilled off from the reaction mass, and the residue was washed with ether and recrystallized twice from dichloroethane; m.p. 219-220°. The substance was dark red in color and difficultly soluble in the ordinary organic solvents.

5.788 mg substance: 9.075 mg AgCl. Found %: Cl 38.79. $C_{13}H_5ONSCl_4$. Calculated %: Cl 38.87.

Amide of Trichlorophenothiazine-1-carboxylic Acid

Gaseous ammonia was passed into a benzene solution of 1 g of the acid chloride of trichlorophenothiazine-1-carboxylic acid until the red coloration disappeared. The yellow crystalline substance which separated was filtered off and washed with water. After having been recrystallized twice from alcohol, it melted with decomposition at 288°.

5.040 mg substance: 6.377 mg AgCl. Found %: Cl 31.30. $C_{13}H_7ON_2SCl_3$. Calculated %: Cl 30.79.

S-Dioxide of the Amide of Trichlorophenothiazine-1-carboxylic Acid

A mixture consisting of 0.5 g of the amide of trichlorophenothiazine-1-carboxylic acid, 25 ml of glacial acetic acid and 4 ml of a 27% aqueous solution of hydrogen peroxide was heated to boiling for 1 hour and then left overnight. The slightly yellowish crystals which settled out were separated and recrystallized from glacial acetic acid.

4.717 mg substance: 5.360 mg AgCl. 4.942 mg substance: 0.321 ml N_2 (21°, 736 mm). Found %: Cl 28.11; N 7.31. $C_{13}H_7O_3N_2SCl_3$. Calculated %: Cl 28.18; N 7.42.

Diethylamide of Trichlorophenothiazine-1-carboxylic Acid

A mixture consisting of 1.4 g of the acid chloride of trichlorophenothiazine-1-carboxylic acid, 0.8 g of diethylamine and 20 ml of acetone was heated to boiling for 5 hours. After distilling off the acetone, a yellowish precipitate with a m.p. of 107-109.5° separated out which was quite soluble in alcohol and in benzene. After it had been recrystallized twice from 70% alcohol, the m.p. was 110.5-111.5°.

5.881 mg substance: 0.351 ml N_2 (18°, 742 mm). 3.721 mg substance: 3.940 mg AgCl. Found %: N 6.83; Cl 26.20. $C_{17}H_{13}N_2OSCl_3$. Calculated %: N 6.97; Cl 26.49.

Acid Chloride of Phenothiazine-1-carboxylic Acid

A mixture consisting of 4 g of phenothiazine-1-carboxylic acid and 10 ml of phosphorus trichloride was heated in a sealed tube at 100° for 20 hours. The phosphorus trichloride was distilled off, the acid chloride was washed with ether, dried in a vacuum desiccator and subjected to further treatment without purification. The weight was 3.5 g.

Azide of Phenothiazine-1-carboxylic Acid

A solution of 3 g of the acid chloride of phenothiazine-1-carboxylic acid in 120 ml of dry dioxane was cooled to 20° and a solution of 2 g of sodium azide in 5 ml of water was added to it in one dose. After standing for 10 minutes, the azide was precipitated by water in the form of a light red powder which was collected, dried and subjected to further treatment without purification. The weight was 3 g.

Phenothiazimidazolone

A suspension of 2.5 g of the azide of phenothiazine-1-carboxylic acid in 20 ml of ethylene glycol was heated on an oil bath, initially at a temperature of 110-120° until nitrogen evolution ceased, and then for 30 minutes at 140-150°. The reaction mass was poured into a large quantity of water, the yellow crystalline substance which precipitated was collected, dried (weight 3 g) and recrystallized twice from glacial acetic acid and then from alcohol. After the three recrystallizations, the phenothiazimidazolone consisted of a colorless crystalline substance with a m.p. of 289-290° which did not change during prolonged boiling with alkalis, with concentrated hydrochloric acid and in a mixture with glacial acetic acid.

4.748 mg substance: 11.280 mg CO_2; 1.419 mg H_2O. 3.730 mg substance: 8.845 mg CO_2; 1.099 mg H_2O. 5.050 mg substance: 0.523 ml N_2 (25°, 744 mm). Found %: C 64.83, 64.71; H 3.34, 3.3; N 11.61. $C_{13}H_8ON_2S$. Calculated %: C 65.00; H 3.33; N 11.66.

SUMMARY

1. The following were synthesized: a) the amide of phenothiazine-1-carboxylic acid, its S-dioxide, the S-dioxides of the butylamide and diethylamide and the p-anisidide of phenothiazine-1-carboxylic acid; b) the hydrazide of phenothiazine-1-carboxylic acid and from it, the corresponding hydrazones, were synthesized with benzaldehyde, p-acetaminobenzaldehyde and with p-hydroxybenzaldehyde.

2. It was demonstrated that during the action on phenothiazine-1-carboxylic acid of excess thionyl chloride or a mixture of phosphoryl chloride and phosphorus pentachloride, the substitution of three hydrogen atoms in the molecule by chlorine occurs. The acid chloride of trichlorophenothiazine-1-carboxylic acid, its amide, diethylamide and the S-dioxide of the amide were prepared.

3. It was proved that when the Curtius rearrangement of the azide of phenothiazine-1-carboxylic acid is conducted, the formation of an imidazole ring occurs.

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• See Consultants Bureau Translation, page 847.

ACETYLENE DERIVATIVES. 165.

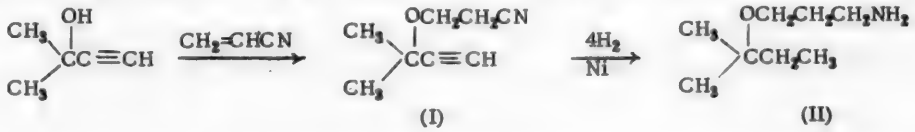
CYANETHYLATION OF ACETYLENIC ALCOHOLS AND GLYCOLS

I. N. Nazarov and G. A. Shvekhgeimer

While the addition of acrylonitrile to saturated alcohols and glycols has been well studied [1], the addition of acrylonitrile to acetylenic alcohols and glycols, with the exception of isolated patents [2] has not been described in the literature. In particular, the addition of acrylonitrile to acetylenic glycols has not been investigated at all, although such glycols are readily available and compounds formed from them by the addition of acrylonitrile can be of interest as intermediate products in the preparation of other valuable substances.

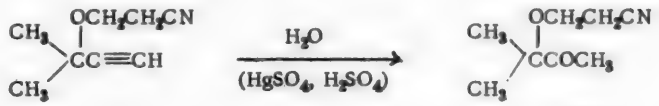
We conducted all the reactions involving the addition of acrylonitrile to unsaturated alcohols and glycols in the presence of a 40% aqueous solution of potassium hydroxide.

During the addition of acrylonitrile to dimethylethynylcarbinol, the β-cyanethyl ether (I) was obtained in a yield of 84%, which on hydrogenation in an autoclave in the presence of Ni catalyst added 4 molecules of hydrogen and yielded the γ-aminopropyl ether of dimethylethylcarbinol (II) in 91% yield:



(I) (II)

The β-cyanethyl ether of dimethylacetylcarbinol (III) was obtained in a yield of 79% by the hydration of the β-cyanethyl ether of dimethylethynylcarbinol (I) in water-dioxane in the presence of mercuric sulfate and sulfuric acid:

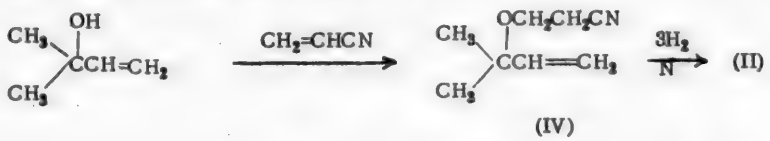


(III)

In the presence of mercuric sulfate alone (without sulfuric acid), the indicated hydration leads to the formation of the β-cyanethyl ether (III) in a yield of only 24%.

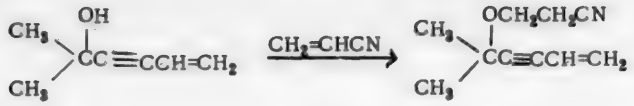
The β-cyanethyl ether (IV) in a yield of 95%, calculating on the basis of the amount of carbinol entering into the reaction, was formed by the action of acrylonitrile on dimethylvinylcarbinol. At the same time, a considerable portion of the unreacted carbinol was recovered.

The γ-aminopropyl ether of dimethylethylcarbinol (II) described above was obtained by the hydrogenation of the β-cyanethyl ether of dimethylvinylcarbinol (IV) in an autoclave.



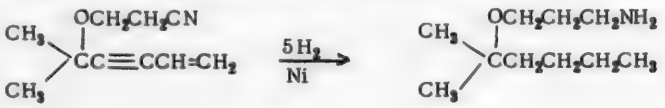
(IV)

Dimethylvinylethynylcarbinol readily adds a molecule of acrylonitrile in the presence of a 40% aqueous solution of potassium hydroxide and forms the β-cyanethyl ether (V) in a yield of 79%:



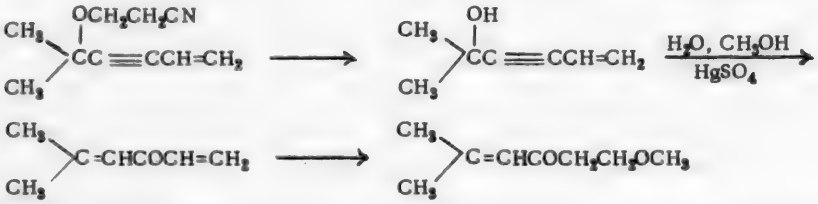
(V)

The β-cyanethyl ether (V) rapidly polymerizes on standing into a transparent yellow colored jelly. The γ-aminopropyl ether of dimethylbutylcarbinol (VI) was obtained in a yield of 94% by the hydrogenation of the β-cyanethyl ether (V) in an autoclave in the presence of Ni catalyst:



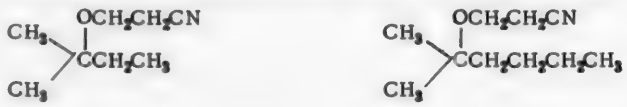
(VI)

At attempt to hydrogenate the β-cyanethyl ether (V) in a water-methanol medium led to the elimination of a molecule of acrylonitrile with subsequent isomerization of the dimethylvinylethynylcarbinol which was formed into β,β-dimethyldivinylketone, the latter added methanol under the conditions of the reaction and was converted into 1-methoxy-5-methyl-4-hexen-3-one [3].



The addition of acrylonitrile to tertiary acetylenic alcohols proceeds considerably more readily than to the corresponding tertiary saturated alcohols which hardly add acrylonitrile at all under ordinary conditions [4].

However, under selected conditions (catalyst, temperature) we succeeded in achieving the addition of acrylonitrile to dimethylethylcarbinol and dimethylbutylcarbinol and in obtaining the corresponding β-cyanethyl ethers (VII) and (VIII) in yields up to 50% (of the carbinol entering into the reaction):



(VII) (VIII)

A great part of the carbinol was recovered unchanged in all these experiments. The above described γ-aminopropyl ethers (II) and (VI) are formed during the hydrogenation of the β-cyanethyl ethers (VII) and VIII).

The simplest acetylenic glycol — 1,4-butynediol — smoothly adds two molecules of acrylonitrile in dioxane solution and forms the di-(β-cyanethyl) ether (IX) in a yield of 88%:

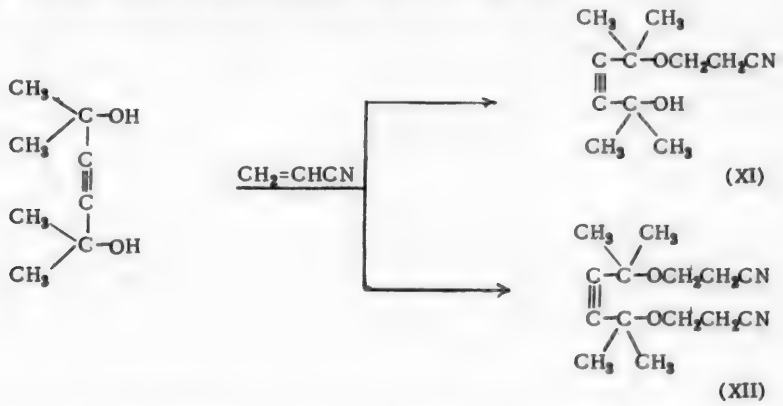
(IX)

In the presence of Raney nickel at 100-110° in an autoclave the di-(β-cyanethyl) ether (IX) rapidly absorbs 6 molecules of hydrogen and is converted into the corresponding di-(γ-aminopropyl) ether (X) in a yield of 84%.

(X)

The hydration of compound (IX) in a water-dioxane medium led to the production of a small quantity of low boiling decomposition products, but the greater portion of the substance resinified.

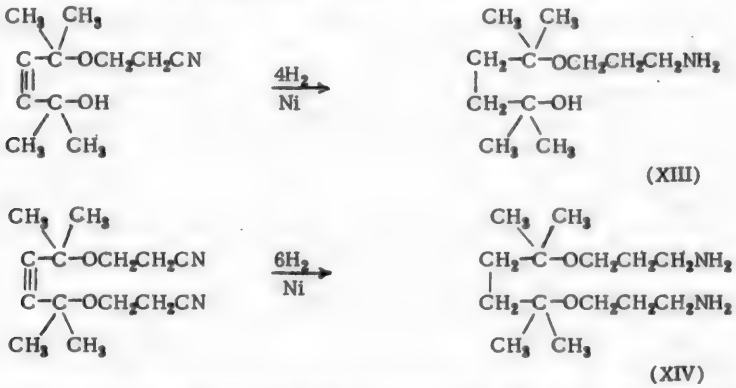
The addition of acrylonitrile to the ditertiary acetylenic glycol – tetramethylbutynediol – in dioxane solution requires heating the reaction mixture at 60-75° for 6 hours. A mixture of the mono- and di-(β-cyanethyl) ethers (XI) and (XIII) in approximately identical quantities was obtained as a result:



(XI)

(XII)

The saturated γ-aminopropyl ethers (XIII) and (XIV) were obtained in excellent yields by the hydrogenation of the ethers (XI) and (XII) in an autoclave at 100-110° over Raney nickel:



(XIII)

(XIV)

The β-cyanethyl ethers described in the present article consist of colorless liquids with a characteristic odor while the γ-aminopropyl ethers obtained by their hydrogenation consist of hygroscopic liquids with a characteristic amine odor which fume in air.

EXPERIMENTAL

Reaction of Acrylonitrile with Dimethylethynylcarbinol. 42 g (0.5 mole) of dimethylethynylcarbinol and 3 g of a 40% aqueous solution of potassium hydroxide were mixed in a three-necked flask supplied with a mechanical stirrer, a dropping funnel and a thermometer. 26.5 g (0.5 mole) of acrylonitrile was gradually added in the course of one hour while the mixture was being stirred energetically. The temperature of the mixture was maintained below 35° by cooling with cold water. After the addition of the acrylonitrile the mixture was stirred at room temperature for 6 hours and then left overnight. On the next day the alkali was neutralized with hydrochloric acid (1:1), the potassium chloride which precipitated was filtered off and the filtrate was vacuum distilled. 57.5 g of the β-cyanethylester of dimethylethynylcarbinol (I) [2b] was obtained:

b.p. 96-96.5° at 18 mm; n_D^{20} 1.4356; d_4^{20} 0.925; MR_D 38.52; calc. 38.54.

13.599 mg sub.: 5.05 ml 0.02 N hyposulfite; 13.816 mg sub.: 5.21 ml 0.02 N hyposulfite. Found %: N 10.30, 10.45. $C_8H_{11}ON$. Calculated %: N 10.22.

The addition of acrylonitrile was conducted analogously in all the other reactions described below.

Hydrogenation of the β-Cyanethyl Ether of Dimethylethynylcarbinol. 25 g (0.182 mole) of the β-cyanethyl ether of dimethylethynylcarbinol (I), 95 ml of methanol saturated with dry ammonia and 25 g of Raney nickel were placed in a 250 ml rotary autoclave. The hydrogenation was conducted for 1 hour 10 minutes at 100-110° and the initial pressure of the hydrogen was 140 atm. The theoretical quantity of hydrogen (16.5 liters) was absorbed. After

the mixture had been cooled, the nickel was filtered off and the filtrate vacuum distilled. 24.2 g of the γ-aminopropyl ether of dimethylethylcarbinol (II) was obtained:

b.p. 68-70° at 14 mm; n_D^{20} 1.4360; d_4^{20} 0.8589; MR_D 44.14; calc. 44.21.

4.505 mg sub.: 0.3715 ml N_2 (19°, 738mm). 4.560 mg sub.: 0.3813 ml N_2 (19°, 748 mm). Found %: N 9.37, 9.44. $C_8H_{19}ON$. Calculated %: N 9.65.

The phenylcarbamide was prepared and had a m.p. of 66-67°.

The other experiments described below which involved the hydrogenation of β-cyanethyl ethers were conducted in a similar manner.

Hydration of the β-Cyanethyl Ether of Dimethylethynylcarbinol. a) 30 g (0.22 mole) of the β-cyanethyl ether of dimethylethynylcarbinol (I), 50 ml of water and 100 ml of freshly distilled dioxane were placed in a three-necked flask supplied with a mechanical stirrer, a reflux condenser and a thermometer. 3 g of mercuric sulfate and 2 drops of concentrated sulfuric acid were added to the homogeneous mixture while it was being stirred vigorously. No appreciable thermal effect was observed. The mixture was heated to 90° and stirred at that temperature for 6 hours. After cooling, the reaction mass was saturated with soda. The upper layer was separated and the lower layer was extracted three times with ether. The product was dried with roasted sodium sulfate and vacuum distilled after distilling off the solvent. 26.8 g of the β-cyanethyl ether of dimethylacetylcarbinol (III) was obtained:

b.p. 132-136° at 18 mm; n_D^{20} 1.4357; d_4^{20} 1.0033; MR_D 40.37; calc. 40.61.

16.217 mg sub.: 5.36 ml 0.02 N hyposulfite. 14.271 mg sub.: 4.78 ml 0.02 N hyposulfite. Found %: N 9.22, 9.27. $C_8H_{13}O_2N$. Calculated %: N 9.03.

b) A mixture of 119 g (9.87 mole) of the ether (I), 200 ml of water, 400 ml of dioxane and 12 g of mercuric sulfate was stirred for 6 hours at 90-91°. 32.3 g of the β-cyanethyl ether of dimethylacetylcarbinol (III) with a b.p. of 130-134° at 17 mm was obtained. 76 g of the starting ether (I) was recovered.

Reaction of Acrylonitrile with Dimethylvinylcarbinol. a) 54 g (0.63 mole) of dimethylvinylcarbinol, 3.5 g of 40% aqueous potassium hydroxide solution and 35 g (0.66 mole) of acrylonitrile were taken in the reaction. 32.5 g of the β-cyanethyl ether of dimethylvinylcarbinol [16] (IV) was obtained:

b.p. 94-96° at 16 mm; n_D^{20} 1.4337; d_4^{20} 0.9056; MR_D 39.98; calc. 40.14.

12.756 mg sub.: 4.79 ml 0.02 N hyposulfite. 12.448 mg sub.: 4.62 ml 0.02 N hyposulfite. Found %: N 10.39, 10.28. $C_8H_{13}ON$. Calculated %: N 10.08.

33 g of the starting carbinol was recovered. The yield of β-cyanethyl ether (IV) was 95%, calculated on the basis of the carbinol which reacted.

b) Reactants: 42 g (0.5 mole) of dimethylvinylcarbinol, 0.6 g of metallic sodium and 26.5 g (0.5 mole) of acrylonitrile. 43.2 g of the ether (IV) with a b.p. of 98 -100° at 24 mm; n_D^{20} 1.4335, was obtained. 8 g of the starting dimethylvinylcarbinol was recovered. The yield of the β-cyanethyl ether (IV) was 78%, calculating on the basis of the carbinol which entered into the reaction.

Hydrogenation of the β-Cyanethyl Ether of Dimethylvinylcarbinol. 21 g (0.151 mole) of the β-cyanethyl ether of dimethylvinylcarbinol (IV), 95 ml of methanol saturated with dry ammonia, and 1.5 g of Raney nickel were taken. The hydrogenation was conducted for 1 hour 45 minutes at 100-110° and the initial hydrogen pressure was 110 atm. The theoretical quantity of hydrogen (10.2 liters) was absorbed.

20.5 g of the above described γ-aminopropyl ether of dimethylethylcarbinol (II) with a b.p. of 56-58° at 7 mm; n_D^{20} 1.4338 was obtained.

The phenylcarbamide was prepared and had a m.p. of 66.5-67°.

Reaction of Acrylonitrile with Dimethylvinylethynylcarbinol. 165 g (1.5 mole) of dimethylvinylethynylcarbinol 10 g of 40% aqueous potassium hydroxide and 53 g (1 mole) of acrylonitrile were taken in the reaction. 129.5 g of the β-cyanethyl ether of dimethylvinylethynylcarbinol was obtained:

b.p. 93-94° at 6 mm; n_D^{20} 1.4710; d_4^{20} 0.9334; MR_D 48.81; calc. 47.31; EMR_D 1.50.

5.345 mg sub.: 0.4038 ml N_2 (20°, 728 mm). 4.235 mg sub.: 0.3293 ml N_2 (20°, 728 mm). Found %: N 8.44, 8.67. $C_{10}H_{13}ON$. Calculated %: N 8.59.

66.5 g of the starting dimethylvinylethynylcarbinol was recovered.

Hydrogenation of the β-Cyanethyl Ether of Dimethylvinylethynylcarbinol. 20 g (0.123 mole) of the β-cyanethyl ether of dimethylvinylethynylcarbinol (V), 105 ml of methyl alcohol saturated with dry ammonia, and 1.5 g of Raney nickel were taken. The hydrogenation was conducted at 90-110° and the initial hydrogen pressure was 135 atm. The theoretical quantity of hydrogen (13.8 liters) was absorbed after 30 minutes. 20.1 g of the γ-aminopropyl ether of dimethylbutylcarbinol (VI) was obtained:

b.p. 102-104° at 18 mm; n_D^{20} 1.4485; d_4^{20} 0.8630; MR_D 53.71; calc. 53.44.

2.913 mg sub.: 0.216 ml N_2 (23°, 748 mm). 3.427 mg sub.: 0.255 ml N_2 (23°, 748 mm). Found %: N 8.42, 8.44. $C_{10}H_{23}ON$. Calculated %: N 8.09;

Reaction of Acrylonitrile with Dimethylethylcarbinol. a) 88 g (1 mole) of dimethylethylcarbinol, 2 g of powdered sodium methylate and 53 g (1 mole) of acrylonitrile were taken in the reaction. The temperature of the mixture gradually rose to 40°. After cessation of the evolution of heat, the stirring was continued for 4 hours more at room temperature and the mixture was then left overnight. The alkali was neutralized with hydrochloric acid (1: 1). 14 g of the β-cyanethyl ether of dimethylethylcarbinol (VII) was obtained:

b.p. 92-97° at 18 mm; n_D^{20} 1.4247; d_4^{20} 0.8981; MR_D 40.12; calc. 40.60.

7.135 mg sub.: 2.61 ml 0.02 N hyposulfite. 13.318 mg sub.: 4.97 ml 0.02 N hyposulfite. Found %: N 10.13, 10.19. $C_8H_{15}ON$. Calculated %: N 9.94.

72.5 g of the starting dimethylethylcarbinol was recovered.

b) 35 g (0.66 mole) of acrylonitrile was added to a mixture of 57 g (0.04 mole) of dimethylethylcarbinol and 4 g of a 40% aqueous solution of potassium hydroxide. No appreciable thermal effect was observed. The mixture was heated to 80° and stirred for 1 hour at this temperature. The reaction mass was cooled after this and the alkali was neutralized with hydrochloric acid (1: 1). 3.6 g of the β-cyanethyl ether of dimethylethylcarbinol with a b.p. of 92-97° at 18 mm; n_D^{20} 1.4247 was obtained.

44 g of the starting dimethylethylcarbinol was recovered.

Hydrogenation of the β-cyanethyl Ether of Dimethylethylcarbinol. 8.8 g (0.063 mole) of the β-cyanethyl ether of dimethylethylcarbinol, 120 ml of methyl alcohol saturated with dry ammonia and 1 g of Raney nickel were taken. The hydrogenation was conducted at 95-105° and the initial hydrogen pressure was 120 atm. The theoretical quantity of hydrogen (2.8 liters) was absorbed in 30 minutes. 8.1 g of the above described γ-aminopropyl ether of dimethylethylcarbinol (II) was obtained:

b.p. 56-58° at 7 mm; n_D^{20} 1.4325.

4.271 mg sub.: 0.3538 ml N_2 (21°, 742 mm). 2.268 mg sub.: 0.1929 ml N_2 (21°, 742 mm). Found %: N 9.39, 9.64. $C_8H_{19}ON$. Calculated %: N 9.65.

The phenylcarbamide was prepared and had a m.p. of 66-67°.

Reaction of Acrylonitrile with Dimethylbutylcarbinol. a) 1.5 g of metallic potassium was added to 120 g (0.71 mole) of dimethylbutylcarbinol. After all the potassium had dissolved, 53 g (1 mole) of acrylonitrile was added to the mixture while it was being stirred vigorously and cooled with cold water. In the course of 2 hours the temperature gradually rose to 45° and then fell to 25°. The alkali was then neutralized with hydrochloric acid (1: 1). 24.3 g of the β-cyanethyl ether of dimethylbutylcarbinol (VIII): was obtained:

b.p. 105-107° at 11 mm; n_D^{20} 1.4306; d_4^{20} 0.8825; MR_D 49.55; calc. 49.84.

b) 85 g (1.6 mole) of acrylonitrile was added to a mixture of 180 g (1.55 mole) of dimethylbutylcarbinol and 12 g of 40% aqueous potassium hydroxide while the mixture was being vigorously stirred. No thermal effect was observed. The mixture was heated to 70° and stirred at this temperature for 2 hours. After cooling, the alkali was neutralized with hydrochloric acid (1: 1) and the mixture was treated in the usual manner. 18 g of the β-cyanethyl ether of dimethylbutylcarbinol was obtained:

b.p. 102-105° at 10 mm; n_D^{20} 1.4308; d_4^{20} 0.8826; MR_D 49.54; calc. 49.84.

4.640 mg sub.: 0.3352 ml N_2 (20°, 724 mm). 3.665 mg sub.: 0.2666 ml N_2 (20°, 731 mm). Found %: N 8.01, 8.00. $C_{10}H_{19}ON$. Calculated %: N 9.28.

155.5 g of the starting carbinol was recovered.

Hydrogenation of the β-Cyanethyl Ether of Dimethylbutylcarbinol. 29 g (0.172 mole) of the β-cyanethyl ether of dimethylbutylcarbinol, 120 ml of methyl alcohol saturated with dry ammonia and 2 g of Raney nickel were taken. The hydrogenation was conducted at 85-95° and the initial hydrogen pressure was 120 atm. The theoretical quantity of hydrogen (7.7 liters) was absorbed in 40 minutes. 27.6 g of the above described γ-aminopropyl ether of dimethylbutylcarbinol (VI) was obtained:

b.p. 78-81° at 6 mm; n_D^{20} 1.4482.

3.125 mg sub.: 0.228 ml N_2 (23°, 748 mm). 3.536 mg sub.: 0.257 ml N_2 (23°, 748 mm). Found %: N 8.28, 8.25. $C_{10}H_{23}ON$. Calculated %: N 8.09.

Reaction of Acrylonitrile with 1,4-Butynediol. 125 g (2.36 mole) of acrylonitrile was gradually added to a mixture of 101 g (1.174 mole) 1,4-butynediol, 150 ml of freshly distilled dioxane and 7 g of a 40% aqueous solution of potassium hydroxide while the mixture was vigorously stirred and cooled with cold water, at such a rate that the temperature of the mixture did not rise above 35°. The stirring was continued at room temperature for 4 hours after the addition of the acrylonitrile and the mixture was then left for 48 hours. The alkali was neutralized with concentrated hydrochloric acid and the product was treated in the usual manner. 216 g of the di-(β-cyanethyl) ether of 1,4-butynediol was obtained in the form of a light yellow viscous oil:

b.p. 189-195° at 3 mm; n_D^{20} 1.4760; d_4^{20} 1.0910; MR_D 49.29; calc. 49.24.

13.541 mg sub.: 5.90 ml 0.02 N hyposulfite. 12.274 mg sub.: 6.16 ml 0.02 N hyposulfite. Found %: N 14.45, 14.43. $C_{10}H_{12}O_2N_2$. Calculated %: N 14.56.

Hydrogenation of the Di-(β-cyanethyl) Ether of 1,4-Butynediol. 19.6 g (0.1 mole) of the di-(β-cyanethyl) ether of 1,4-butynediol (IX), 90 ml of methyl alcohol saturated with dry ammonia and 2.5 g of Raney nickel were taken. The hydrogenation was conducted at 90-105° and the initial hydrogen pressure was 100 atm. The theoretical quantity of hydrogen (13.5 liters) was absorbed in 20 minutes. 17.5 g of the di-(γ-aminopropyl) ether of 1,4-butanediol (X) was obtained:

b.p. 134-136° at 4 mm; n_D^{20} 1.4618; d_4^{20} 0.9620; MR_D 58.59; calc. 58.51.

12.317 mg sub.: 1.143 ml N_2 (22°, 757 mm). 9.636 mg sub.: 1.126 ml N_2 (22°, 757 mm). Found %: N 13.63, 13.44. $C_{10}H_{24}O_2N_2$. Calculated %: N 13.72.

Reaction of Acrylonitrile with Tetramethylbutynediol. 50 g (0.94 mole) of acrylonitrile was added to a mixture of 59 g (0.415 mole) of tetramethylbutynediol, 200 ml of freshly distilled dioxane and 4 g of a 40% aqueous solution of potassium hydroxide while the mixture was vigorously stirred. No thermal effect was observed. The mixture was stirred for 5 hours at 60-70° and for one hour at 70-75°, after which it was left to stand for 40 hours. The alkali was neutralized with concentrated hydrochloric acid and the product was treated in the usual manner The following fractions were obtained after fivefold vacuum distillation: 1) 111-112° at 3 mm (37.6 g), 2) 112-132° at 2.5 mm (7.9 g), 3) - 142 146° at 2.5 mm (32.1 g).

The first fraction consisted of the mono-β-cyanethyl ether of tetramethylbutynediol (XI):

b.p. 111-112° at 3 mm; n_D^{20} 1.4530; d_4^{20} 0.9758; MR_D 54.01; calc. 53.92.

9.45 mg sub.: 23.44 mg CO_2; 7.65 mg H_2O. 10.19 mg sub.: 25.42 mg CO_2; 8.05 mg H_2O. Found %: C 67.70, 67.92; H 9.05, 8.84. $C_{11}H_{17}O_2N$. Calculated %: C 67.69; H 8.72.

The third fraction consisted of the di-(β-cyanethyl) ether of tetramethylbutynediol (XII); it was a colorless viscous liquid which crystallized on standing:

b.p. 142-146° at 2.5 mm; m.p. about 25°; n_D^{20} 1.4553; d_4^{20} 0.9915; MR_D 67.91; calc. 67.71.

5.795 mg sub.: 14.285 mg CO_2; 4.230 mg H_2O. 5.515 mg sub.: 13.567 mg CO_2; 3.890 mg H_2O. Found %: C 67.27, 67.13; H 8.17, 7.89. $C_{14}H_{20}O_2N_2$. Calculated %: C 67.74; H 8.07.

Hydrogenation of the Mono-β-cyanethyl Ether of Tetramethylbutynediol. 19.5 g (0.1 mole) of the mono-β-cyanethyl ether of tetramethylbutynediol (XI), 100 ml of methyl alcohol saturated with dry ammonia and 1 g of Raney nickel were taken. The hydrogenation was conducted at 90-100° and an initial hydrogen pressure of 130 atm. The theoretical quantity of hydrogen (8.95 liters) was absorbed in one hour. 18 g of the mono-γ-aminopropyl ether of tetramethylbutanediol was obtained:

b.p. 91-94° at 4 mm; n_D^{20} 1.4587; d_4^{20} 0.9321; MR_D 59.50; calc. 59.59.

4.850 mg sub.: 0.2936 ml N_2 (21°, 726 mm). 3.910 mg sub.: 0.2411 ml N_2 (21°, 726 mm). Found %: N 6.71, 6.86. $C_{11}H_{25}O_2N$. Calculated %: N 6.89.

The phenylcarbamide was prepared and had a m.p. of 181.5-182.5°.

Hydrogenation of the Di-(β-cyanethyl) Ether of Tetramethylbutynediol. 24.8 g (0.1 mole) of the di-(β-cyanethyl) ether of tetramethylbutynediol (XII), 90 ml of methyl alcohol saturated with dry ammonia and 1.5 g of Raney nickel were taken. The hydrogenation was conducted at 90 100° and an initial hydrogen pressure of 135 atm. The theoretical quantity of hydrogen (13.5 liters) was absorbed in one hour. 21 g of the di-(γ-aminopropyl) ether of tetramethylbutanediol (XIV) was obtained:

b.p. 136-138° at 3.5 mm; n_D^{20} 1.4752; d_4^{20} 0.9539; MR_D 76.77; calc. 76.98.

12.725 mg sub.: 5.60 ml 0.02 N hyposulfite. 12.968 mg sub.: 5.72 ml 0.02 N hyposulfite. Found %: N 10.95, 10.95. $C_{14}H_{32}O_2N_2$. Calculated %: N 10.77.

The phenylcarbamide was prepared and had a m.p. of 115-116° (from alcohol).

SUMMARY

1. The addition of acrylonitrile to dimethylethynylcarbinol, dimethylvinylcarbinol, dimethylvinylethynylcarbinol, 1,4 butynediol, tetramethylbutynediol and the preparation of the corresponding β nitrilethyl ethers in high yields was described.

2. The possibility of adding acrylonitrile to tertiary saturated alcohols under ordinary conditions was demonstrated.

3. The corresponding γ-aminopropyl ethers were obtained in high yields by the hydrogenation of the β-cyanethyl ethers.

4. The β-cyanethyl ether of dimethylethynylcarbinol formed the β-cyanethyl ether of dimethylacetylcarbinol in a yield of 79% during hydration in the presence of mercuric sulfate and sulfuric acid.

5. Attempts to hydrate the β-cyanethyl ethers of dimethylvinylethynylcarbinol and 1,4-butynediol were not successful.

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[2] a) American Cynamid Co., Brit. Pat. 544421, C. A. 36, 6548 (1942); b) H. Bruson, U. S. Patent 2280790; C. A. 36, 5588 (1942); c) E. Schwoegler, U. S. Patent 2403686; C. A. 40, 6499 (1946).

[3] I. N. Nazarov and co-workers, Bull, Acad. Sci. USSR, Div. Chem. Sci., 1944, 65; 1946, 633; 1947, 51.

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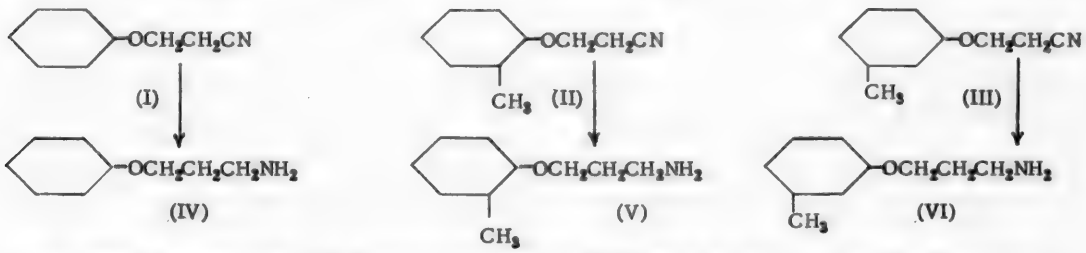
THE CYANETHYLATION OF CYCLIC AND HETEROCYCLIC ALCOHOLS AND AMINES.

HYDROGENATION AND ALCOHOLYSIS OF THE CYANETHYLATION PRODUCTS

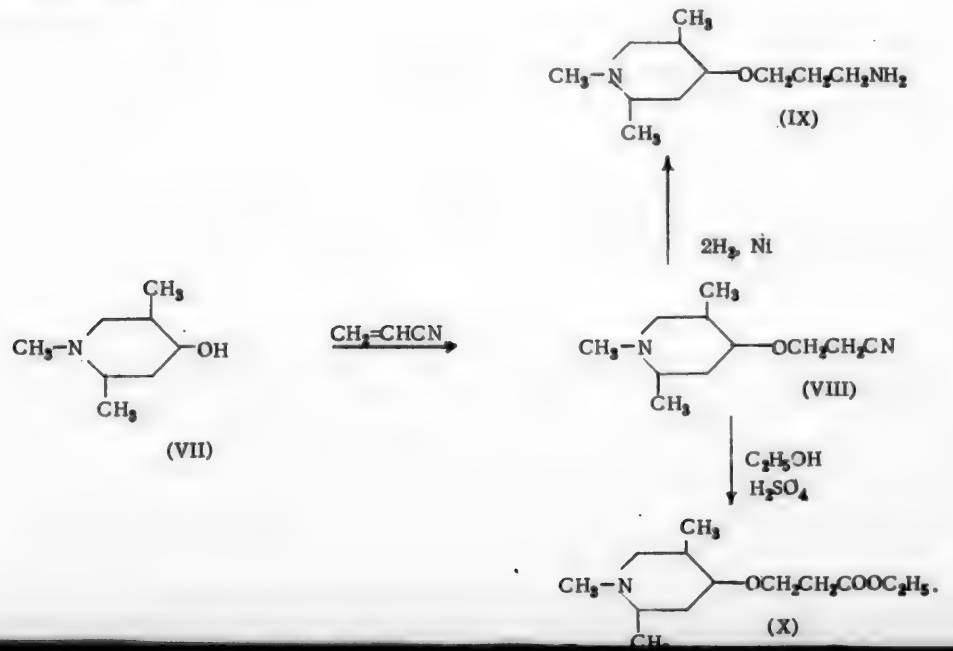
I. N. Nazarov and G. A. Shvekhgeimer

The addition of acrylonitrile to cyclic and heterocyclic alcohols has hardly been investigated at all until recently. In particular, data concerning the addition of acrylonitrile to alcohols of the cyclohexanol series are almost entirely absent in the literature. The addition of acrylonitrile to γ-piperidols, which are important starting materials for the synthesis of physiologically active compounds, has not been studied at all.

The addition of acrylonitrile to cyclohexanol, 2- and 3-methylcyclohexanols, 1,2,5-trimethyl-4-piperidol and also the hydrogenation and alcoholysis of the compounds thereby obtained are described in the present article. By the action of acrylonitrile on cyclohexanol, 2-methycyclohexanol and 3-methylcyclohexanol in the presence of a 40% aqueous solution of potassium hydroxide, the corresponding β-cyanethyl ethers (I), (II) and (III) were obtained in yields greater than 90%; during the hydrogenation of the latter with nickel catalyst in the presence of dry ammonia the γ-aminopropyl ethers (IV), (V) and (VI) were formed in yields of 95-96%:

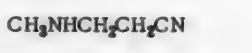


The action of acrylonitrile on 1,2,5-trimethyl-4-piperidol (VII) leads to the formation of the β-cyanethyl ether (VIII) in almost quantitative yield (calculating on the basis of the piperidol which entered into the reaction). The latter (VIII) forms the γ-aminopropyl ether (IX) in a yield of 96% on hydrogenation with nickel catalyst in the presence of ammonia, and is converted in a yield of 80% to the β-carbethoxyethyl ether (X) by alcoholysis in the presence of sulfuric acid:

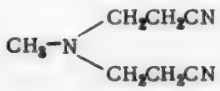


The alcoholysis of the cyanethyl ether (VIII) proceeds with considerable difficulty in comparison with ordinary nitriles and requires prolonged heating (18 hours) at a temperature not below 90°. We also conducted the addition of acrylonitrile to methylamine, dimethylamine and 2,5-dimethyl-4-piperidone with the object of studying the hydrogenation of the products thereby formed. Primary aliphatic amines, as is well known [1], add one molecule of acrylonitrile very readily, while the introduction of a secondmolecule requires extreme conditions (heating in a sealed ampoule) and in spite of all this still does not result in obtaining high yields of alkyl-di-(β-cyan ethyl)-amines.

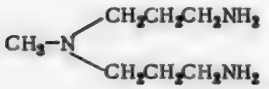
By heating acrylonitrile with methyl-β-cyanethylamine (XI) for 16 hours at 90° we obtained methyl-di(β-cyanethyl)-amine (XII) in a yield of 89%; by hydrogenating the latter in the presence of nickel catalyst and gaseous dry ammonia the methyldi-(γ-aminopropyl)-amine (XIII) was formed in a yield of 73%. 1-Methyl-1,5-diazacyclooctane (XIV), formed via cleavage of ammonia from the triamine (XIII) is also obtained at the same time as the product of a side reaction.



(XI)



(XII)



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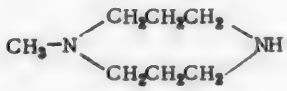

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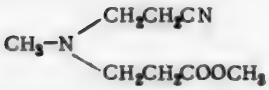
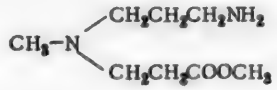


(XV)

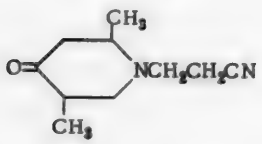


(XVI)

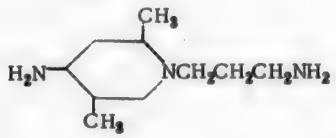
During the reaction of methyl-β-cyanethyl amine (XI) with methyl acrylate for 5 days at room temperature, methyl-β-cyanethyl-β-carbomethoxyethylamine (XV) was obtained in a yield of 92%; during the hydrogenation of the latter the amino-ether (XVI) should be formed. During the attempt to vacuum distil the hydrogenation product, however, it was converted into a polymerized mass and we did not succeed in isolating it in this manner. The β-cyanethyl derivatives (XVII) and (XVIII) obtained by the addition of acrylonitrile to dimethylamine and 2,5-dimethyl-4-piperidone, are converted by hydrogenation in the presence of nickel catalyst and dry gaseous ammonia into the corresponding γ-aminopropyl derivatives (XIX) and (XX) in a yield of about 80%.

(XVII)

(XIX)



(XVIII)



(XX)

Under these conditions, the hydrogenation of the nitrile group in compound (XVIII) is accompanied by reduction of the aminated carbonyl group.

EXPERIMENTAL

Addition of Acrylonitrile to Cyclohexanol. 105 g (1.98 mole) of acrylonitrile was added to a mixture of 193 g (1.93 mole) of cyclohexanol and 14 g of a 40% aqueous solution of potassium hydroxide while the mixture was being stirred vigorously. The temperature of the mixture was maintained below 30° by cooling with cold water and regulating the rate of addition of acrylonitrile. The stirring was continued at room temperature for 6 hours after the addition of the acrylonitrile and then the mixture was left overnight. The alkali was neutralized with hydrochloric acid (1:1), the potassium chloride which precipitated was filtered off, and the filtrate was vacuum distilled. 48 g of cyclohexanol was recovered and 208 g of the β-cyanethyl ether of cyclohexanol (I) was obtained:

b.p. 130-132° at 20 mm; n_D^{20} 1.4586; d_4^{20} 0.9674; MR_D 42.99; calc. 43.02.

10.139 mg sub.: 3.31 ml 0.02 N hyposulfite. 11.861 mg sub.: 3.57 ml 0.02 N hyposulfite. Found %: N 8.99, 8.74. $C_9H_{15}ON$. Calculated %: N 9.15.

The other experiments involving the addition of acrylonitrile were conducted analogously (see below).

Hydrogenation of the β-Cyanethyl Ether of Cyclohexanol. 35 g (0.23 mole) of the β-cyanethyl ether of cyclohexanol (I), 120 ml of methyl alcohol saturated with dry ammonia and 2 g of Raney nickel were taken. The hydrogenation was conducted at 95-105° and the initial hydrogen pressure was 145 atm. The theoretical quantity of hydrogen (10.4 liter) was absorbed in 1 hour and 15 minutes. The product was filtered off from the catalyst and vacuum distilled. 34.5 g of the γ-aminopropyl ether of cyclohexanol (IV) was obtained:

b.p. 72-74° at 4.5 mm; n_D^{20} 1.4646; d_4^{20} 0.9281; MR_D 46.73; calc. 46.63 [2].

3.508 mg sub.: 0.284 ml N_2 (23°, 743 mm). 3.270 mg sub.: 0.266 ml N_2 (23°, 732 mm). Found %: N 9.13, 9.18. $C_9H_{19}ON$. Calculated %: N 8.92.

The phenylcarbamide with a m.p. of 101.5-102.5° (from benzene) was obtained.

Addition of Acrylonitrile to 2-Methylcyclohexanol. 142 g (1.24 mole) of 2-methylcyclohexanol, 10 g of a 40% aqueous solution of potassium hydroxide and 70 g (1.32 mole) of acrylonitrile were taken for the reaction. 42 g of the starting 2-methylcyclohexanol and 137.5 g of the β-cyanethyl ether of 2-methylcyclohexanol (II) were obtained:

b.p. 134-137° at 18 mm; n_D^{20} 1.4564; d_4^{20} 0.9502; MR_D 47.81; calc. 47.64.

9.270 mg sub.: 2.20 ml 0.02 N hyposulfite. 5.750 mg sub.: 1.76 ml 0.02 N hyposulfite. Found %: N 8.18, 8.31. $C_{10}H_{17}ON$. Calculated %: N 8.38.

Hydrogenation of the β-Cyanethyl Ether of 2-Methylcyclohexanol. 34.5 g (0.2 mole) of the β-cyanethyl ether of 2-methylcyclohexanol (II), 130 ml of methyl alcohol saturated with dry ammonia and 2 g of Raney nickel were taken. The hydrogenation was conducted at 90-100° and the initial hydrogen pressure was 150 atm. The theoretical quantity of hydrogen (8.95 liters) was absorbed in 1 hour 20 minutes. The reaction mass was cooled, the nickel filtered off and the filtrate vacuum distilled. After distilling off the methanol 34 g of the γ-aminopropyl ether of 2-methylcyclohexanol (V) was obtained:

b.p. 73-74.5° at 3.5 mm; n_D^{20} 1.4603; d_4^{20} 0.9115; MR_D 51.39; calc. 51.24.

7.537 mg sub.: 0.554 ml N_2 (22°, 754 mm). 3.581 mg sub.: 0.264 ml N_2 (22°, 750 mm). Found %: N 8.34, 8.42. $C_{10}H_{21}ON$. Calculated %: N 8.18.

The phenylcarbamide with a m.p. of 96-98° was prepared.

Reaction of 3-Methylcyclohexanol with Acrylonitrile. 114 g (1 mole) of 3-methylcyclohexanol, 7 g of a 40% aqueous solution of potassium hydroxide and 53 g (1 mole) of acrylonitrile were taken. 37.5 g of the starting 3-methylcyclohexanol and 109.5 of the β-cyanethyl ether of 3-methylcyclohexanol (III) were obtained:

b.p. 133-136° at 16 mm; n_D^{20} 1.4529; d_4^{20} 0.9458; MR_D 47.82; calc. 47.64.

7.975 mg sub.: 2.38 ml 0.02 N hyposulfite. 7.370 mg sub.: 2.25 ml 0.02 N hyposulfite. Found %: N 8.44, 8.63. $C_{10}H_{17}ON$. Calculated %: N 8.38.

Hydrogenation of the β-Cyanethyl Ether of 3-Methylcyclohexanol. 27.6 g (0.16 mole) of the β-cyanethyl ether of 3-methylcyclohexanol (III), 120 ml of methyl alcohol saturated with dry ammonia and 1.5 g of Raney nickel were taken. The hydrogenation was conducted at 90-100° and the initial hydrogen pressure was 100 atm. The theoretical quantity of hydrogen (7.2 liter) was absorbed in 45 minutes. 26.9 g of the γ-aminopropyl ether of 3-methylcyclohexanol (VI) was obtained:

b.p. 76-78° at 4 mm; n_D^{20} 1.4599; d_4^{20} 0.9118; MR_D 51.35; calc. 51.24.

5.245 mg sub.: 0.392 ml N_2 (22°, 748 mm). 3.640 mg sub.: 0.274 ml N_2 (21°, 749 mm). Found %: N 8.53, 8.39. $C_{10}H_{21}ON$. Calculated %: N 8.18.

Reaction of Acrylonitrile with 1,2,5-Trimethyl-4-piperidol. 17 g (0.32 mole) of acrylonitrile was added to a vigorously stirred mixture of 45 g (0.314 mole) of 1,2,5-trimethyl-4-piperidol (VII) and 3 g of a 40% aqueous solution of potassium hydroxide. The temperature spontaneously rose to 35° and fell to 21° after an hour. The stirring was continued at room temperature for 4 hours after this, and the mixture was then left overnight. The alkali was

neutralized with an equivalent quantity of hydrochloric acid, the potassium chloride which settled out was filtered off, and the filtrate vacuum distilled. 14.1 g of the starting piperidol (VII) and 42 g of the β-cyanethyl ether of 1,2,5-trimethyl-4-piperidol (VIII) in the form of a colorless oil with a characteristic amine odor was obtained:

b.p. 117° at 4 mm; n_D^{20} 1.4635; d_4^{20} 0.9661; MR_D 55.97; calc. 56.20.

9.940 mg sub.: 5.07 ml 0.02 N hyposulfite. 11.059 mg sub.: 5.67 ml 0.02 N hyposulfite. Found %: N 14.25, 14.50. $C_{11}H_{12}ON_2$. Calculated %: N 14.28.

The picrate with a m.p. of 111-113° (from a mixture of alcohol and acetone) was obtained.

Hydrogenation of the β-Cyanethyl Ether of 1,2,5-Trimethyl-4-piperidol. 19.6 g (0.1 mole) of the β-cyanethyl ether of 1,2,5-trimethyl-4-piperidol (VIII), 100 ml of methyl alcohol saturated with dry ammonia and 2 g of Raney nickel were taken. The hydrogenation was conducted at 90-100° and the initial hydrogen pressure was 125 atm. The theoretical quantity of hydrogen (4.5 liters) was absorbed in 35 minutes. 19.2 g of the γ-aminopropyl ether of 1,2,5-trimethyl-4-piperidol (IX) was obtained:

b.p. 116-118° at 8 mm; n_D^{20} 1.4680; d_4^{20} 0.9315; MR_D 59.80; calc. 59.68.

21.383 mg sub.: 6.50 ml 0.02 N hyposulfite. 17.038 mg sub.: 9.53 ml 0.02 N hyposulfite. Found %: N 14.05, 13.90. $C_{11}H_{24}ON_2$. Calculated %: N 14.00.

The picrate with a m.p. of 147-149° (from alcohol) was obtained.

Alcoholysis of the β-Cyanethyl Ether of 1,2,5-Trimethyl-4-piperidol. a) A mixture of 20 g (0.1 mole) of the β-cyanethyl ether of 1,2,5-trimethyl-4-piperidol (VIII), 50 ml of ethyl alcohol and 30 g of concentrated sulfuric acid was stirred for 18 hours at 90° (the mixture boiled at this temperature). After cooling, 100 ml of water was poured in; the product was neutralized with soda, salted out with potash, extracted with ether, dried with sodium sulfate and vacuum distilled. 20.2 g of the β-carbethoxyethyl ether of 1,2,5-trimethyl-4-piperidol (X) was obtained:

b.p. 109-110° at 4 mm; n_D^{20} 1.4504; d_4^{20} 0.9807; MR_D 66.64; calc. 67.27.

4.955 mg sub.: 0.239 ml N_2 (20°, 751 mm). 4.680 mg sub.: 0.235 ml N_2 (20°, 751 mm). Found %: N 5.53, 5.78. $C_{13}H_{25}O_3N$. Calculated %: N 5.76.

The hydrochloride with a m.p. of 93.5-95° was obtained.

b) Alcoholysis did not occur when a mixture of 40 g of the β-cyanethyl ether (VIII), 100 ml of methyl alcohol and 50 g of concentrated sulfuric acid was heated for 8 hours at 70°, and the β-cyanethyl ether (VIII) was recovered in a quantity of 24 g.

Reaction of Acrylonitrile with Methylamine. To a mixture of 122 g (4 moles) of methylamine in 700 ml methanol which was vigorously stirred and cooled with ice water, 208 g (4 moles) of acrylonitrile was added over a period of 2 hours at such a rate the temperature of the mixture did not rise above 30°. The stirring was continued at room temperature for 10 hours after addition of the acrylonitrile. After distilling off the methyl alcohol and vacuum distilling the product, 255.5 g of the β-cyanethylmethylamine (XI) was obtained:

b.p. 86° at 25 mm; n_D^{20} 1.4320 [3].

In addition, 54 g of di-(β-cyanethyl)-methylamine (XII) was obtained:

b.p. 162-164° at 6 mm; n_D^{20} 1.4606.

Reaction of Acrylonitrile with β-Cyanethylmethylamine. A mixture of 21.5 g (0.25 mole) of β-cyanethylmethylamine (XI) and 16 g (0.3 mole) of acrylonitrile was heated with a reflux condenser at 90° for 16 hours. 31.2 g of di-(β-cyanethyl)-methylamine (XII) was obtained:

b.p. 159.5-160° at 5 mm; n_D^{20} 1.4612 [3].

Hydrogenation of Di-(β-cyanethyl)-methylamine. 13.7 g (0.1 mole) of di-(β-cyanethyl)methylamine (XII), 60 ml of methyl alcohol saturated with dry ammonia and 1 g of Raney nickel were taken. The hydrogenation was conducted at 90-100° and an initial hydrogen pressure of 100 atm. The theoretical quantity of hydrogen (9 liters) was absorbed in 1.5 hours. 10.6 of di-(γ-aminopropyl)-methylamine (XIII) was obtained:

b.p. 81-83° at 4 mm; n_D^{20} 1.4753; d_4^{20} 0.9023; MR_D 45.26; calc. 45.31.

6.183 mg sub.: 1.558 ml N_2 (20°, 754 mm). 4.556 mg sub.: 1.164 ml N_2 (22°, 753 mm). Found %: N 29.13, 29.29. $C_7H_{19}N_3$. Calculated %: N 28.97.

1-Methyl-1,5-diazacyclooctane (XIV) in the form of the hydrochloride with a m.p. of 189.5-190° (from alcohol) was isolated from the low boiling fraction.

2.585 mg sub.: 0.3862 ml N_2 (20°, 736 mm). 2.345 mg sub.: 0.3519 ml N_2 (20°, 744 mm). Found %: N 16.84, 17.13. $C_7H_{17}N_2Cl$. Calculated %: N 17.02.

Reaction of β-Cyanethylmethylamine with Methyl Acrylate. 21.5 g (0.25 mole) of the methyl ether of acrylic acid was added in small portions to 21 g (0.25 mole) of β-cyanethylmethylamine (XI) which was being stirred and cooled with ice water. The temperature of the mixture did not rise above 30°. After the spontaneous evolution of heat had ceased, the flask was closed and left at room temperature for 5 days. 39.3 g of β-carbomethoxyethyl-β-cyanethylmethylamine (XV) was obtained:

b.p. 133° at 6 mm; 114° at 4.5 mm; n_D^{20} 1.4507; d_4^{20} 1.0338; MR_D 44.25; calc. 44.56.

7.216 mg sub.: 1.020 ml N_2 (21°, 756 mm). 8.725 mg sub.: 1.254 ml N_2 (21°, 756 mm). Found %: N 16.70, 16.60. $C_8H_{14}O_2N_2$. Calculated %: N 16.47.

The picrate was obtained with a m.p. of 108-109° (from alcohol).

Hydrogenation of β-Carbomethoxyethyl-β-cyanethylmethylamine. 34 g (0.2 mole) of the nitrile ether (XV), 50 ml of methyl alcohol saturated with dry ammonia and 2 g of Raney nickel were placed in a 152 ml rotary autoclave. The hydrogenation was conducted at 90-100° and the initial hydrogen pressure was 100 atm. The theoretical quantity of hydrogen (9 liters) was absorbed after 1.5 hours. The mixture was cooled, the nickel filtered off and the methyl alcohol eliminated in a vacuum on a water bath, the temperature of which did not rise about 50°. Under these conditions the liquid in the flask acquired a more and more viscous consistency and finally was converted into a rubber-like, dark brown, polymerized mass.

Reaction of Acrylonitrile with Dimethylamine. 318 g (6 moles) of acrylonitrile was added to a solution of 270 g (6 moles) of dimethylamine in 400 g of methyl alcohol which was being stirred vigorously and cooled with ice water, at such a rate that the temperature of the mixture did not exceed 30°. After cessation of the spontaneous evolution of heat the mixture was stirred at 40-55° for 1 hour and then left overnight. After distilling off the methyl alcohol and vacuum distilling the product, 566.5 g of β-dimethylaminopropionitrile (XVII) was obtained:

b.p. 60-61° at 10 mm, 68° at 18 mm; n_D^{20} 1.4282 [4, 5].

Hydrogenation of β-Dimethylaminopropionitrile. 200 g (2 mole) of β-dimethylaminopropionitrile (XVII), 1220 ml of methyl alcohol, saturated with dry ammonia and 10 g of Raney nickel were taken. The hydrogenation was conducted at 80-90° and the initial hydrogen pressure was 85 atm. The theoretical quantity of hydrogen was absorbed in 45 minutes. 134 g of γ-dimethylaminopropylamine (XIX) with a b.p. of 131-134° at 758 mm; n_D^{20} 1.4398, was obtained by repeated fractional distillation.

57 g of the hydrochloride of γ-dimethylaminopropylamine with a m.p. of 183-184° (from methyl alcohol) [4, 5] was isolated in addition by saturating the methyl alcohol driven off and the low boiling fractions with dry hydrogen chloride.

Reaction of Acrylonitrile with 2,5-Dimethyl-4-piperidone. A mixture of 127 g (1 mole) of 2,5-dimethyl-4-piperidone and 53 g (1 mole) of acrylonitrile was heated at 95-97° for 3 hours and then left overnight at room temperature. 104 g of the starting piperidone and 31.2 g of 1-(β-cyanethyl)-2,5-dimethyl-4-piperidone (XVIII) in the form of a colorless viscous oil were obtained:

b.p. 143-145° at 5.5 mm; n_D^{20} 1.4841; d_4^{20} 1.0345; MR_D 49.79; calc. 49.95.

2.055 mg sub.: 0.278 ml N_2 (21°, 740 mm). 2.870 mg sub.: 0.394 ml N_2 (21°, 740 mm). Found %: N 15.30, 15.50. $C_{10}H_{18}ON_2$. Calculated %: N 15.55.

Hydrochloride m.p. 166.5-167° (from acetone).

Picrate m.p. 136-137° (from acetone).

Hydrogenation of 1-(β-Cyanethyl)-2,5-dimethyl-4-piperidone. 13.3 g (0.075 mole) of 1-(β-cyanethyl)-2,5-dimethyl-4-piperidone (XVIII), 100 ml of methyl alcohol saturated with dry ammonia and 1.5 g of Raney nickel were taken. The hydrogenation was conducted at 100-110° and the initial hydrogen pressure was 100 atm. The theoretical quantity of hydrogen (5 liters) was absorbed in one hour. 10.6 g of 1-(γ-aminopropyl)-2,5-dimethyl-4-amino piperidine (XX) was obtained:

b.p. 108-110° at 3.5 mm; n_D^{20} 1.4917; d_4^{20} 0.9475; MR_D 56.72; calc. 56.96.

4.535 mg sub.: 0.896 ml N_2 (20°, 751 mm). 4.595 mg sub.: 0.892 ml N_2 (20°, 754 mm). Found %: N 22.79, 22.49. $C_{16}H_{23}N_3$. Calculated %: N 22.70.

The picrate with a m.p. of 227.5-228.5° (from a mixture of alcohol and acetone) was obtained.

SUMMARY

1. By the addition of acrylonitrile to cyclohexanol, 2- and 3-methylcyclohexanols, and also to 1,2,5-trimethyl-4-piperidol, the corresponding β-cyanethyl ethers (I), (II), (III) and (VIII) were obtained in yields greater than 90%; by the hydrogenation of the latter under pressure in the presence of nickel catalyst and dry gaseous ammonia the γ-aminopropyl ethers (IV), (V), (VI), and (IX) were obtained in yields of 95%.

2. The carbethoxyethylether of piperidol (X) was also obtained during the alcoholysis of the β-cyanethyl ether (VIII).

3. The addition of methyl-β-cyanethylamine (XI) to acrylonitrile and methyl acrylate was accomplished and compounds (XII) and (XV) were thus obtained in high yields.

4. The hydrogenation of the β-cyanethyl derivatives (XII), (XVII), and (XVIII) in the presence of ammonia was described and the corresponding γ-aminopropyl derivatives (XIII), (XIX) and (XX) were obtained in high yields.

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PYRIDINE DYE DERIVATIVES OF DIPHENYL

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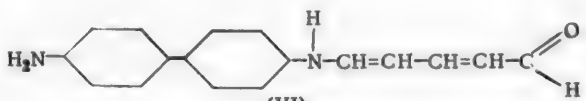
Pyridine dye derivatives of diphenyl have hardly been studied at all. We obtained and investigated four symmetrical dyes (I), (II), (III), (IV) and the quaternary pyridine salts corresponding to them (see table) by the reaction of the 2,4-dinitrochlorophenylate of pyridine with benzidine, 4-aminodiphenyl, 4-nitro-4'-aminodiphenyl and the p-aminochlorodiphenylate of pyridine.

The dyes obtained, in contrast to the phenyl derivatives investigated by us [1], were decomposed with difficulty in solutions. On heating the dry substance to a determined temperature the original color disappears; the dye is decomposed in the course of 15-30 minutes without melting. Only the derivatives of the p-aminochlorodiphenylate of pyridine (II) and 4-nitro-4'-aminodiphenyl (IV) decomposed according to the usual pattern [2] for an amine and the corresponding quaternary pyridine salt. Independent compounds were formed from the derivatives of benzidine and 4-aminodiphenyl, the composition of which agrees with that of the starting dye.

The yellow substance obtained after heating the benzidine derivative (VI) in the dry form at 180° was investigated in detail. The finely crystalline powder with a m.p. of 273° when recrystallized from water crystallized with the solvent. It crystallized from methyl alcohol in the form of shiny yellow plates with a m.p. of 277°. The substance began to sublime during heating to 280-200° and the sublimation continued even after fusion; the sublimed substance had a bright orange color and did not contain solvent, but rapdily yellowed in the air and attracted moisture; it did not melt on heating to 300°. The presence of three amine groups was determined by diazotization. After boiling the diazo solution two substances were isolated – the p-hydroxychlorodiphenylate of pyridine (V) and 4,4-dihydroxydiphenyl (with a m.p. of 270°).

(V)

The yellow substance did not react with alkali in the cold and it was only after boiling it with an alkaline solution that a red substance – the product of the cleavage of the p-aminochlorodiphenylate of pyridine (VI) and benzidine was isolated.



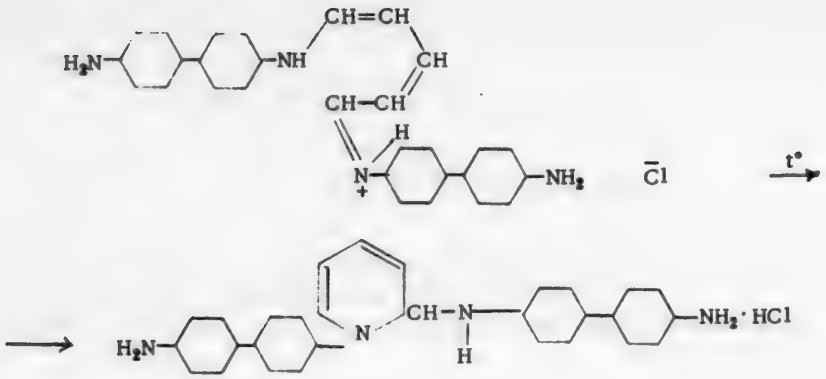
(VI)

The capacity to sublime and the behavior toward alkali are evidence of the considerable stability of the substance.

The substance condenses with the 2,4-dinitrochlorophenylate of pyridine and two dyes are thereby formed – the derivatives of the p-aminochlorodiphenylate of pyridine and benzidine, but the reaction proceeds slowly and the dyes are obtained in low yield.

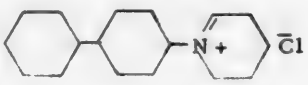
Although the diazotization determined three amine groups, on the basis of which it could be assumed that the yellow substance consisted of a molecular compound of the quaternary pyridine salt – the p-aminochlorodiphenylate of pyridine and benzidine, the great stability of the substance and also the absence of molecular compounds in the thermal decomposition products of the two other dyes (II), and (IV), raise doubts concerning the correctness of such an assumption.

It is highly probable that isomerization of the molecule without elimination of an amine proceeds during the heating of the dye:



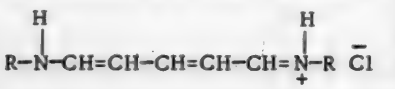
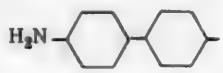
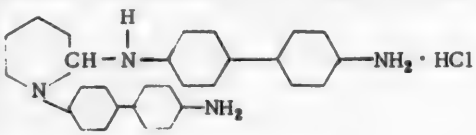
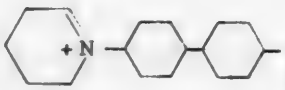
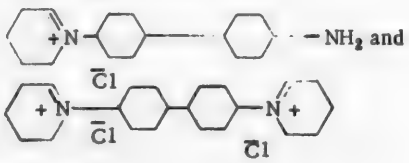
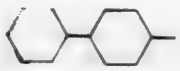
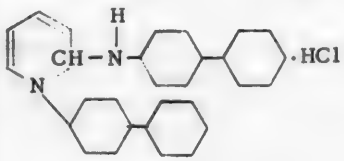
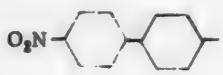
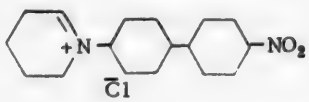
The substance formed – the hydrochloride of (N-p-aminodiphenyl-α-hydro-4,4'-diaminodiphenyl)-pyridine – is decomposed during diazotization into the p-aminochlorodiphenylate of pyridine and benzidine which are then diazotized.

The yellow substance obtained by heating the diphenyl derivative (III) is less stable, in contrast to the benzidine derivative. It decomposes during recrystallization from water into the chlorodiphenylate (VII) and 4-aminodiphenyl.



(VII)

The diverse behavior of the diphenyl derivatives during heating, as well as their color, is associated with the character of the amine radicals – the greater the basicity of the amine, the more stable the dye corresponding to it and the deeper its color (see the table).

Significance of R in the dye formula 		λmax. (in mμ)		Decomposition temperature (in °C)	Salts obtained by the termal decomposition of the dye
		in ethyl alcohol	in ethyl alcohol and HCl		
(I)		535	526	180	
(II)		510	510	230	
(III)		516	522	150	
(IV)		•	530	135	

• The dye hydrolyzes in neutral solution.

EXPERIMENTAL

Chloride of 1,5-Bis-(4,4'-aminodiphenyl)-pentadiene-1,3-ylidiene-5

An alcoholic solution of benzidine (5.2 g in 15 ml) was poured into a solution of 4 g of the 2,4-dinitrochlorophenylate of pyridine in 10 ml of ethyl alcohol; a rich cherry-red coloration at once appeared and the mixture crystallized. After the solution had been heated for 5 minutes on a boiling water bath and had been cooled, the dye was filtered off, washed several times with warm acetone to free it from the dinitroaniline, with hot water to free itfrom the quaternary salt, and with a small quantity of alcohol and ether. 6 g (89%) of the thus purified dye was obtained. It consisted of completely homogeneous crystals under the microscope. 2 g of the dye was heated with 150 ml of ethyl alcohol, but most of it (1.7 g) did not dissolve. After the solution had stood for a day, 0.01 g of dye in the form of a finely crystalline green powder that did not melt on heating to 300° was obtained. It contained chlorine. It crystallized with the solvent; this was difficult to determine quantitatively, since the dye became hygroscopic after elimination of the solvent.

Found %: N 10.72, 10.68. $C_{29}H_{27}N_4Cl \cdot 1\ 1/4C_2H_5OH$. Calculated %: N 10.69.

Decomposition of the Dye. 1 g of the dye in 150 ml of alcohol was heated for 8 hours with 3 ml of hydrochloric acid (d 1.19) on a boiling water bath. The dye which did not decompose (0.45 g) was filtered off, the alcohol distilled off and the brown precipitate which remained was recrystallized from water. 0.4 g of a yellow substance, soluble in hot water and poorly soluble in alcohol was obtained; the substance did not dissolve in ether, contained chlorine, and crystallized with the solvent, m.p. 273°. Benzidine was not detected. The content of nitrogen in the yellow substance was higher than in the p-aminochlorodiphenylate of pyridine, which should be formed during the decomposition of the dye according to the usual pattern.

Found %: N 10.56, 10.57. $C_{17}H_{15}N_2Cl \cdot H_2O$. Calculated %: N 9.31. $C_{29}H_{27}N_4Cl \cdot 4H_2O$. Calculated %: N 10.40

The dye was more readily decomposed in water in the presence of hydrochloric acid, but still slowly. It was noted during the attempt to determine the melting point of the dye that the dye became brown at 160-180° and did not change on heating to 270°. 2.2 g of a light-brown substance was obtained after heating 2.3 g of the dye at 170-180° for 15-20 minutes in a desiccator. A yellow, finely crystalline powder with m.p. 273° was obtained after crystallization from 250 ml of water. The melting point of a mixed sample with the substance obtained after decomposition of the dye in alcohol was not depressed. It crystallized from methyl alcohol in the form of shiny yellow needles, m.p. 277°. It contained solvent. 1 g of the substance was sublimed in a covered glass crucible. The bright-yellow sublimate, which did not melt on heating to 300°, rapidly attracted moisture on exposure to air and became yellow.

Found %: N 11.69, 11.70; Cl 7.11, 7.38. Calculated %: N 11.56; Cl 7.33.

1 g of the substance consumed 10.4 ml of 0.5 N $NaNO_2$ (with a $K_{instability} = 1.1$) on diazotization, which corresponded to the presence of three amine groups. The diazo solution was heated until the evolution of nitrogen bubbles ceased. After cooling, an orange precipitate settled out which recrystallized from water in the form of a finely crystalline powder, slightly tinged with a rose color (0.6 g); it consisted of heterogeneous crystals under the microscope. The substance was treated with ether several times and was twice recrystallized from aqueous alcohol (4: 1). 0.2 g of material, which consisted of colorless needles under the microscope, was obtained. It did not melt on heating to 300° and contained solvent.

Found %: N 4.29, 4.15. $C_{17}H_{14}NOCl \cdot 3H_2O$. Calculated %: N 4.15.

A colorless substance was isolated from the ethereal solution which agreed in its melting point (270°) with that of 4,4'-dihydroxydiphenyl.

1 g of the yellow substance, dissolved by heating in 100 ml of water, was poured into a hot solution of 5 ml of 25% sodium hydroxide. A red color at once appeared and a brownish-red precipitate settled out. The mixture was boiled for a half hour and filtered while hot. 0.5 g of a brownish-red precipitate was obtained which was carefully washed with water until the alkali was eliminated. The precipitate was heated with 200 ml of acetone and 0.3 g dissolved. After a day an insignificant quantity of a brown substance that did not contain chlorine precipitated. An intense red color appeared during the addition to an acetone or alcohol solution of drops of hydrochloric acid. A solution of the substance in acetic acid was violet colored (unstable). The substance contained solvent. Its properties agreed with those of the alkaline cleavage product of a quaternary pyridine salt.

Found %: N 8.81, 8.77. $C_{17}H_{16}N_2O \cdot CH_3COCH_3$. Calculated %: N 8.69.

After concentration and decolorizing the aqueous filtrate, benzidene was isolated.

Condensation of the Yellow Substance with the 2,4-Dinitrochlorophenylate of Pyridine. A solution of 3.5 g of the dinitrochlorophenylate of pyridine in 15 ml of methyl alcohol was added to a solution of 5 g of the yellow substance in 190 ml of methyl alcohol. During the mixing of the hot solutions a weak red color appeared. In 4-5 minutes after beginning the heating of the mixture, green crystals settled on the walls of the flask. Heating was continued for 20 minutes on a boiling water bath. The precipitate which formed was washed on the filter with ether, hot water, acetone and again with ether. 2.43 g of a mixture of dyes was obtained. In view of the poor solubility of the dyes in organic solvents, attempts to separate them by crystallization were unsuccessful. We succeeded in separating the dyes only by decomposing one of them during prolonged boiling of the mixture in acidified water. The undecomposed preparation was separated by centrifuging, and washed with water, acetone and ether. The dye contained solvent.

Found %: N 7.78, 7.75. $C_{39}H_{33}N_4Cl_3 \cdot 2CH_3OH$. Calculated %: N 7.70.

Thermal Decomposition of the Chloride of 1,5-Bis-(4-aminochlorodiphenylate)-pentadiene-1,3-ylidene-5. 0.4 g of the dye (which did not decompose when the mixture was boiled in water) was heated in a desiccator at 230° for 30 minutes. A precipitate that was completely insoluble in water was probably a residue (0.1 g) of carbonized dye. The solution was completely boiled down on a water bath and the brown substance which remained was dissolved in alcohol from which it did not settle out and from which it was, consequently, precipitated with acetone. The precipitate operation was repeated twice. 0.06 g of light yellow substance was obtained, which was quite soluble in water and did not melt on heating to 300°.

Found %: N 7.03, 7.09; Cl 15.97. $C_{22}H_{18}N_2Cl_2 \cdot C_2H_5OH$. Calculated %: N 6.56; Cl 16.63.

The high analytical results for nitrogen and the low results for chlorine can be explained by admixture of the p-aminochlorodiphenylate of pyridine which is formed along with the dipyridine salt, but which we could not isolate.

Chloride of 1,5-Bis-(4-aminodiphenyl)-pentadiene-1,3-ylidene-5

A mixture of 2 g of the 2,4-dinitrochlorophenylate of pyridine and 1.94 g of 4-aminodiphenyl [3] in 20 ml of ethyl alcohol was heated for 10 minutes on a water bath. After cooling, the mixture was mixed with ether, the precipitate was washed on the filter with ether and water and recrystallized from ethyl alcohol. 1.5 g (56.8%) of the dye was obtained in the form of fine, silky, red crystals with a bluish-green sheen. They consisted of violet plates under the microscope. M.p. 151-152°. The crystals contained solvent.

Found %: N 6.15, 6.17. $C_{29}H_{25}N_2Cl \cdot 1/2C_2H_5OH$. Calculated %: N 6.09.

Thermal Decomposition of the Dye. 0.6 g of the dye was heated in a desiccator for 1 hour at 150°. 0.57 g of an orange product was obtained which was recrystallized from water. Upon dissolving it in hot water the separation of a brown oil was observed which proved to be 4-aminodiphenyl. 0.4 g of a yellow flaky substance was obtained from the aqueous solution, which darkened on heating above 150°, was quite soluble in alcohol, water and acetone; and was insoluble in ether. It contained solvent. A test for chlorine was positive. It did not react with alkali without heating. The substance was almost completely decomposed by repeated crystallization from water into 4-aminodiphenyl and the chlorodiphenylate of pyridine. A small residue was recrystallized from ethyl alcohol in the presence of carbon and washed well with ether.

Found %: N 5.93, 5.89. $C_{29}H_{25}N_2Cl \cdot C_2H_5OH$. Calculated %: N 5.80.

The aqueous solution after separation of the yellow substance was decolorized with carbon and concentrated to 2-3 ml. Coarse needle-shaped colorless crystals (0.12 g) settled out after several hours. The substance contained chlorine, crystallized with the solvent, and melted at 110-112°.

Found %: N 5.01. $C_{17}H_{14}NCl \cdot H_2O$. Calculated %: N 4.90.

Repeated purification of the substance was conducted by reprecipitating it from alcohol with ether. A finely crystalline product was obtained which contained solvent and melted at 112°.

Found %: N 4.48. $C_{17}H_{14}NCl \cdot C_2H_5OH$. Calculated %: N 4.46.

The chlorodiphenylate of pyridine was quite soluble in water and alcohol and less soluble in acetone. A red color appeared and a brown precipitate settled out during the addition of alkali to an aqueous solution. After recrystallization from acetone, a red powder which contained solvent was obtained.

Found %: N 5.22, 5.16. $C_{17}H_{15}NO \cdot 1/2CH_3COCH_3$. Calculated %: N 5.03.

Chloride of 1,5-Bis-(4-nitro-4'-aminodiphenyl)-pentadiene-1,3-ylidene-5

A mixture of 3 g of 4-nitro-4'-aminodiphenyl and 2.7 g of the 2,4-dinitrochlorophenylate of pyridine in 50 ml of ethyl alcohol was heated on a boiling water bath for 50 minutes. 1.6 g (39.9%) of the dye was obtained and washed with acetone and water. 0.2 g of the dye was recrystallized from 50 ml of ethyl alcohol. 0.1 g of fine green crystals with a metallic sheen was obtained. The dye was readily precipitated from alcoholic solution by mild acidification with hydrochloric acid. During prolonged heating of the alcoholic solution or during considerable dilution with alcohol the orange-red color disappeared and the solution became yellow. The dye was soluble in acetic acid and crystallized very well from it.

With the object of increasing the yield of dye the condensation of the starting materials was conducted in the presence of pyridine; 1 g of amine was dissolved by heating in 7 ml of pyridine, and a hot solution of 1 g of the initial salt in 10 ml of ethyl alcohol was poured into this solution. A red color at once appeared and in 2-3 minutes after the beginning of the heating the mixture crystallized. On the following day the mixture was diluted with acetone, and the precipitate on the filter was washed with warm acetone, hot water, ether, and again with acetone. 1.25 g (93.5%) of a dark-green, finely crystalline dye was obtained. A portion of it was recrystallized from alcohol. It crystallized with the solvent.

Found %: N 9.84, 9.89. $C_{29}H_{22}N_4O_4Cl \cdot C_2H_5OH$. Calculated %: N 9.78.

Decomposition of the Dye. After heating 1 g of the dye for an hour at 135° the initial color disappeared and a mixture of orange and brown crystals was formed. After treating the mixture with hot water 0.55 g of 4-nitro-4'-aminodiphenyl (m.p. 200°) was obtained. A quaternary salt – the chloride of the p-nitrodiphenylate of pyridine – was obtained in the form of fine light-yellow needles from the mother liquor after separation of the amine, decolorizing the solution with carbon and concentrating it. The material contained chlorine. A test for presence of solvent was positive.

Found %: N 7.85, 7.78. $C_{17}H_{13}N_3O_3Cl \cdot C_2H_5OH$. Calculated %: N 7.81.

The quaternary salt was readily soluble in water, and was cleaved by alkali in the cold with the formation of a red substance.

SUMMARY

1. The following three pyridine dyes which had not been described previously were synthesized: the chloride of 1,5-bis-(4-aminodiphenyl)-pentadiene-1,3-ylidene-5, the chloride of 1,5-bis-(4-nitro-4'-aminodiphenyl)-pentadiene-1,3-ylidene,5, and the chloride of 1,5-bis-(p-aminochlorodiphenylate of pyridine)-pentadiene-1,3-ylidene-5.

2. A hypothesis was proposed to the effect that during the heating of the dye derivatives of benzidine and of 4-aminodiphenyl, isomeric transformation of the molecule without amine cleavage occurs.

3. The following four quaternary pyridine salts which had not been described previously were prepared: 4,4'-bis-(pyridine chloride)-N,N'-diphenyl, the chlorodiphenylate of pyridine, the 4-nitrochlorodiphenylate of pyridine, and the 4-hydroxychlorodiphenylate of pyridine.

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INVESTIGATION OF ORGANIC ISOCYNATES

III. REACTION OF AROMATIC ISOCYANATES WITH HALOGENS

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As early as 1887 Gumpert [1] described the labile addition products formed by the action of chlorine or bromine on a solution of phenylisocyanate in chloroform.

According to Gumpert, these substances are readily decomposed into their components and evolve iodine from a solution of iodide salts; the bromine addition product is converted by heating into 4-bromophenylisocyanate with evolution of hydrogen bromide. These data were confirmed by Curtius [2, 3] in 1895 and 1913 as relates to the bromine addition product. Curtius also carried out another method of preparation – the reaction of benzazide with bromine in chloroform and gave a more precise description of the properties of the substance: m.p. 144°, it sublimates without decomposition during careful heating, and is smoothly converted into 4-bromophenylisocyanate with evolution of HBr only when its vapors are superheated.

Siefken confirmed in a recently published work [4] on the basis of experiments involving the chlorination of phenylisocyanate in tetrachloroethane that Gumpert had not clarified the nature of the reaction products of chlorine and phenylisocyanate. Actually, the acid chloride of phenylcarbamic acid is initially formed and later on compounds containing chlorine in the benzene ring.

In our experiments involving the reaction of chlorine and bromine with phenyl, 4-tolyl-, 4-nitrophenyl- and 1-naphthylisocyanate we did not succeed in observing the addition products described by Gumpert and Curtius. A colorless crystalline compound is evolved by the action of chlorine and bromine on a solution of phenylisocyanate in chloroform, which, according to the analysis, contains 2 atoms of halogen per isocyanate molecule. The compounds obtained yield a weak coloration with a solution of potassium iodide and starch which disappears as a result of the addition of 1-2 drops of 0.1 N thiosulfate. One equivalent of acid was detected by titration with alkali. When the substance is heated, it is converted into halogen-substituted phenylisocyanates; with alcohol it yields esters of halogenphenylcarbamic acid and with concentrated sulfuric acid 4-chloro- and 4-bromoanilines. A substance identical with that obtained by the action of bromine on phenylisocyanate and agreeing in properties with that described by Curtius, was formed by the addition of the elements of hydrogen bromide to 4-bromophenylisocyanate and, consequently, actually consists of the acid bromide of 4-bromophenylcarbamic acid.

It is of interest that the phenyl-, 4-tolyl- and 4-nitrophenylisocyanates did not yield reaction products with equimolecular quantities of chlorine in carbon tetrachloride.

If a small quantity of dry hydrogen chloride is introduced into a solution of phenylisocyanate and chlorine in carbon tetrachloride, then a precipitate of the acid chloride of 4-chlorophenylcarbamic acid settles out. In contrast to the isocyanates of the benzene series, 1-naphthylisocyanate in carbon tetrachloride forms the acid chloride of 4-chloro-1-naphthylcarbamic acid directly by the action of chlorine. The difference in the behavior of phenyl- and 1-naphthylisocyanates is also observed during their reaction with sulfuryl chloride. Phenylisocyanate does not react appreciably and a mixture of the substances can be separated by fractional distillation at normal pressure; 1-naphthylisocyanate yields the acid chloride of 4-chloro-1-naphthylcarbamic acid even while being cooled.

Thus, in agreement with Siefken, the reaction of halogens with arylisocyanates at low temperatures ought to be considered as a halogenation of arylcarbamic acid derivatives. The substituent initially enters in the para-position which is usually also observed in other cases of halogenation of acylaminoderivatives. The presence in the reaction mass of hydrogen halide is necessary to initiate the reaction. The latter, evidently, can be formed either as a result of reaction with the solvent (chlorination and bromination of phenylisocyanate in chloroform and tetrachloroethane) or as a result of reaction with a molecule of isocyanate (chlorination of 1-naphthylisocyanate in carbon tetrachloride).

Previously, during the investigation of the transformations of arylisocyanates under the action of added aluminum chloride, we presented considerations concerning the orienting influence of the isocyanate group during the introduction of new substituents into the aromatic nucleus [5]. The isocyanate and diacylamine groups were on the same level as the halogens, combining the para- and ortho-orientation with deactivation of the aromatic nucleus.

It seemed possible to trace the orienting influence of the isocyanate group in experiments involving the chlorination of isocyanates by raising the temperature. It is well known that at a temperature above 115°, as a consequence of the thermal dissociation of the acid chloride of phenylcarbamic acid, hydrogen chloride does not yield addition products with phenylisocyanate [6], and one could expect substitution here as a result of the direct action of chlorine on arylisocyanate. The chlorination of phenylisocyanate at 120-130° confirmed this hypothesis. The process proceeds many times more slowly than in chloroform at ordinary temperature. Not only mono-, but also polychloro- derivatives, are formed, along with a large quantity of phenylisocyanate which does not react. The phenyl-, 4-chlorophenyl-, 2,4-dichlorophenyl- and 2,4,6-trichlorophenyl- isocyanates were detected in the reaction mixture. It was noted that pure phenylisocyanate, free from traces of N,N'-diphenylurea – a constant admixture formed even on brief contact with moist air – absorbs chlorine appreciably more slowly. The chlorination of phenylisocyanate preparations, free from diphenylurea and containing 1% of this substance, for 6 hours in a strong stream of gaseous chlorine under identical conditions led to a weight increase in the first case of 12.5 and in the second of 29.0%.

The catalytic activity of diphenylurea under these conditions can be explained by a greater chlorination rate of this substance or the product of its reaction with phenylisocyanate – 1,3,5-triphenylbiuret, and the decomposition of the chloro-derivative of the latter with the reformation of diphenylurea and chlorine-substituted phenylisocyanate. The formation of 1,3,5-triphenylbiuret from N,N'-diphenylurea and phenylisocyanate and its thermal decomposition in the starting material has been described in the literature [7]. The possibility of bringing about the process according to the following scheme was confirmed by special experiments:

$$RNCO + R'NHCONHR' \rightarrow RNHCONR'CONHR' \rightarrow RNHCONHR' + R'NCO.$$

Phenylisocyanate was obtained by heating N,N'-diphenylurea with 1- or 2-naphthylisocyanates, and was distilled off from the reaction mixture. It is of interest to note that phenylisocyanate was also obtained by heating acetanilide with 1-naphthylisocyanate. Such an exchange must apparently also be a consequence of the rearrangement of the intermediate compound N-acetyl-N-phenyl-N'-naphthylurea.

In contrast to phenylisocyanate, 1-naphthylisocyanate at 160-170° vigorously absorbs chlorine with the formation of 4-chloro- and 2,4-dichloro-1-naphthylisocyanates and products of more profound chlorination. The rate and direction of the reaction under these circumstances must be explained in connection with the greater stability and reactivity of the nuclear-substituted acid chloride of 1-naphthylcarbamic acid.

EXPERIMENTAL

Reaction of Phenylisocyanate with Chlorine in Chloroform. 10 g of phenylisocyanate was introduced into 80.8 ml of a solution of 5.96 g of chlorine in chloroform. After 12 hours it was filtered, washed with chloroform, and dried in a vacuum desiccator. Colorless crystals were formed; yield 4.57 g.

Found %: HCl 19.07, 19.39. $C_7H_5ONCl_2$. Calculated %: HCl 19.21.

A portion of the substance was introduced into concentrated sulfuric acid, diluted with water, neutralized and steam distilled. M.p. 69.6-70.8°. A mixture with 4-chloroaniline (m.p. 68.8-70.8°) melted at 69.0-70.8°.

Reaction of Isocyanate with Chlorine in Carbon Tetrachloride. 1) A weighed sample of isocyanate (phenyl-4-tolyl-, 4-nitrophenylisocyanate) was placed in a solution of an equimolecular quantity of chlorine in carbon tetrachloride. After about 12 hours the solvent and chlorine were eliminated under a vacuum. The residue did not contain chlorine and consisted of unchanged isocyanate. In the experiment with phenylisocyanate the latter was identified in the form of the methyl ester of phenylcarbamic acid, m.p. 44.4-46.4°; in the experiment with 4-tolylisocyanate – in the form of the butyl ester of 4-tolylcarbamic acid, m.p. 60.4-62.0°; in the experiment with 4-nitrophenylisocyanate – as the same, m.p. 55.6-57.0°.

2) 20.0 g of phenylisocyanate was placed in 165 ml of a solution of 12.09 g of chlorine in carbon tetrachloride and a stream of dry hydrogen chloride was passed over the surface of the solution for 7 minutes. After 12 hours

the colorless crystalline precipitate was filtered, washed with carbon tetrachloride and dried in a vacuum at room temperature. 39.5 g of a substance, identical with the acid chloride of 4-chlorophenylcarbamic acid obtained by conducting the reaction in chloroform solution, was obtained.

3) 46.2 ml of a solution of 3.88 g of chlorine in carbon tetrachloride was added to 9.21 g of 1-naphthylisocyanate at 5°. In 20 minutes a white crystalline precipitate had settled out, which was filtered, pressed out and dried in a vacuum at room temperature. Weight 2.10 g. M.p. 86-89° with decomposition.

Found %: HCl 13.07. $C_{11}H_7ONCl_2$. Calculated %: HCl 15.20.

The methyl ester of 4-chloro-1-naphthylcarbamic acid with m.p. 148.8-149.7° was formed with methyl ether. A mixture with the substance obtained from 4-chloro-1-naphthylisocyanate and methyl alcohol (m.p. 149.3-149.7°) melted at 149.0-149.7°.

Reaction of Phenylisocyanate with Bromine. 20 g of bromine was added in drops to a solution of 10 g of phenylisocyanate in 50 ml of chloroform which was being cooled with an ice mixture. It was filtered, washed with chloroform and dried on a clay plate in a vacuum over potassium hydroxide. 10.23 g of a colorless crystalline substance with m.p. 134-144° (with decomposition [3]) was obtained.

Found %: HBr 27.23, 27.20. $C_7H_5ONBr_2$. Calculated %: HBr 29.03.

A portion of the material was placed while cool in concentrated sulfuric acid, the sulfuric acid solution was poured out on ice, neutralized with alkali and the 4-bromoaniline, m.p. 62.4-63.4° (66° [8]) was steam distilled.

Another portion of the material (0.1 g) was placed in 1 ml of absolute alcohol, and 0.35 g of pyridine was added. The ethyl ester of 4-bromocarbamic acid with m.p. 78.6-79.4° (81° [3]) precipitated during dilution with water. 10 g of the substance was heated for 3 hours at 155-160° and vacuum distilled. 3.1 g of 4-bromophenylisocyanate with m.p. 37-41° (42° [3]) was obtained.

Dry hydrogen bromide was passed into a solution of 4-bromophenylisocyanate in chloroform. The precipitate was filtered, washed, and dried over potassium hydroxide. Colorless crystals with m.p. 135-145° were obtained. A mixture with the substance obtained by the action of bromine on phenylisocyanate, melted at 134-145°.

Chlorination of Phenylisocyanate. 1) With the object of excluding traces of admixed N,N'-diphenylurea or of 1,3,5-triphenylbiuret, 60 g of freshly prepared phenylisocyanate was treated for 1 hour with phosgene at 150°, the temperature was lowered to 120-130° and a strong stream of chlorine was passed into it for 6 hours. The weight of the chlorinated mass was 67.5 g. The following fractions were obtained by distillation: 1st 162-175° (50.6 g); 2nd 175-200° (5.20 g); 3rd 200-247° (7.4 g).

2) 60 g of freshly prepared phenylisocyanate and 0.6 g of N,N'-diphenylurea were chlorinated for 6 hours at 120-130°. The weight of the chlorinated mass was 77.98 g. Distillation yielded the following fractions: 1st 162-175° (32.39 g), 2nd 175-225° (22.54 g) 3rd 225-255° (12.09 g). The following were isolated from the 1st and 2nd fractions by subsequent fractional distillation and crystallization: phenylisocyanate, 4-chlorophenylisocyanate (m.p. 30-32°; it yielded the methyl ester of 4-chlorophenylcarbamic acid, m.p. 114.4-116.8° with methyl alcohol; 4-chloroaniline, m.p. 69.4-70.8° by decomposition with sulfuric acid; and 4-chloroacetanilide, m.p. 176-177° with acetic anhydride), 2,4-dichlorophenylisocyanate (m.p. 57.0-58.8°; it yielded 2,4-dichloroanilide, m.p. 61.4-62.4° by decomposition with sulfuric acid and 2,4-dichloroacetanilide, m.p. 145-146° with acetic anhydride). 2,4,6-Trichloroaniline (m.p. 74.8-75.8°; it yields 2,4,6-trichloroacetanilide, m.p. 205.0-206.6° with acetic anhydride) was isolated from the 3rd fraction after decomposition with sulfuric acid, dilution with water and steam distillation. None of the substances isolated gave melting point depressions with substances obtained by known methods. No amines were detected in the distillate obtained by steam distillation of the sulfamines obtained by the decomposition of the 1st and 2nd fractions with concentrated sulfuric acid, which, according to Beilshtein and Kurbatov [9], indicates the absence of o-chloroaniline.

Chlorination of 1-Naphthylisocyanate. A stream of chlorine was passed into 35.07 g of 1-naphthylisocyanate at 160-170° until the weight became equal to 42 g. Vacuum distillation at 4 mm yielded the following fractions: 1st 138-143° (9.70 g); 2nd 143-156° (14.09 g); 3rd 156-175° (14.76 g). The 1st fraction primarily consisted of 1-naphthylisocyanate, while 4-chloro-1-naphthylisocyanate was isolated from the 2nd fraction by recrystallization from benzene. A portion of the material of the 3rd fraction was placed into concentrated sulfuric acid. A sulfate was isolated by dilution of the sulfuric acid solution with water and ice, from which a substance with a m.p. 79.5-80.5° was obtained by steam distillation in acidic medium; after recrystallization from ethyl alcohol it melted at 80.7-81.7° (m.p. of 2,4-dichloro-1-naphthylamine 82° [10], 83-84° [11]). It yielded an acetyl derivative with acetic

anhydride – needles with m.p. 217.9-218.2° (from diluted ethyl alcohol). A mixture with 2,4-dichloro-1-acetylaminonaphthalene, obtained by chlorinating 1-acetylaminonaphthalene (m.p. 217.8-218.5°) melted at 217.9-218.5°. Alkali was added to the portion of the material remaining after separation of the 2,4-dichloro-1-naphthylamine and distillation was resumed. A product with m.p. 93-95° passed over into the distillate. A substance with m.p. 188.9-189.5° was obtained after acetylation with acetic anhydride. A mixture with 4-chloro-1-acetylaminonaphthalene, m.p. 189.5-189.8°, obtained from 1-acetylaminonaphthalene with potassium chlorate, melted at 188.4-188.9°.

Exchange Reaction of Naphthylisocyanate with N,N'-Diphenylurea and Acetanilide 1) 10.6 g of N,N'-diphenylurea and 16.9 g of 1-naphthylisocyanate were heated in a distillation flask. 4.9 g of phenylisocyanate (41.1% of the theoretical quantity, calculating on the basis of the 1-naphthylisocyanate) was distilled off into the receiving flask.

2) 3.91 g of phenylisocyanate (65.7% of the theoretical) was obtained from 10.6 g of N,N'-diphenylurea and 8.45 g of 1-naphthylisocyanate, analogously to the preceding.

3) 1.20 g of phenylisocyanate (50.4% of the theoretical) was obtained from 4.24 g of N,N'-diphenylurea and 3.38 g of 2-naphthylisocyanate.

4) 0.49 g of phenylisocyanate was obtained from 6.75 g of acetanilide and 8.45 g of 1-naphthylisocyanate. The phenylisocyanate was identified in the form of the methyl ester of phenylcarbamic acid.

SUMMARY

1. It was established that, contrary to the data of Gumpert and Curtius, arylisocyanates do not form addition products with chlorine and with bromine.

2. The chlorination of phenyl and 1-naphthylisocyanates was investigated.

3. It was established that phenylisocyanate is obtained by heating 1- and 2-naphthylisocyanates with N,N'-diphenylurea and acetanilide.

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REACTION OF N,N'-BIS-(HALOMAGNESIUM)-ARYLAMINES WITH ESTERS AND ACID HALIDES

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It is well known that organomagnesium derivatives of aromatic amines react with esters of carboxylic acids with the formation of arylamides [1]. This reaction has recently found application for the synthesis of polyenes, for example Vitamin A [2] and the arylamides of β-hydroxy acids [3].

Calculated on the basis of the amount of ester taken, arylamides are obtained in excellent yield, while only half of the quantity of amine taken is converted into arylamide. During the preparation of the arylmagnesium halide-amine, the latter often precipitates and a considerable quantity of dry ether is consumed in order to dissolve it.

As our experiments demonstrated, these drawbacks of the method can readily be eliminated if the reaction is conducted with organodimagnesium derivatives of aromatic amines in accordance with the following scheme:

$$RCOOR' + ArN(MgX)_2 \longrightarrow Mg(OR')X + RC(OMgX)=NAr \xrightarrow{HCl} MgXCl + RCONHAr.$$

At the same time the N,N-bis-(halomagnesium)-arylamine reacts with the ester group in equimolecular proportions, and thereby guarantees maximum utilization of the amine taken for the reaction.

Experiment No.	Ester	N,N-Bis-(bromomagnesium)-arylamine	Arylamide	Yield (in %)	Melting point	
					our data	according to the literature data [6]
1	$CH_3COOC_2H_5$	$C_6H_5N(MgBr)_2$	$CH_3CONHC_6H_5$	83.1*	113-114*	113-114*
2	$CH_3(CH_2)_2COOC_2H_5$	$C_6H_5N(MgBr)_2$	$CH_3(CH_2)_2CONHC_6H_5$	81.1	95.5	95- 96
3	$C_6H_5COOC_2H_5$	$C_6H_5N(MgBr)_2$	$C_6H_5CONHC_6H_5$	83.3	161-162	162
4	$C_6H_5COOC_2H_5$	β-$C_{10}H_7N(MgBr)_2$	$C_6H_5CONHC_{10}H_7$-β	88.4	160-161	161
5	$C_6H_5COOC_2H_5$	o-$CH_3C_6H_4N(MgBr)_2$	$C_6H_5CONHC_6H_4CH_3$-o	97.3	143-144	142-143
6	$(COOC_2H_5)_2$	$C_6H_5N(MgBr)_2$	$(CONHC_6H_5)_2$	85	244-245	245
7	$C_2H_5OCOCH_2CH_2COOC_2H_5$	$C_6H_5N(MgBr)_2$	$C_6H_5NHCOCH_2CH_2CONHC_6H_5$	98.7	222-225	226
8	$C_6H_5CH=CHCOOC_2H_5$	$C_6H_5N(MgBr)_2$	$C_6H_5CH=CHCONHC_6H_5$	83.6	151-152	150-151
9	$CH_2ClCOOC_2H_5$	$C_6H_5N(MgBr)_2$	$CH_2ClCONHC_6H_5$	71.5	133	134-135
10	$(C_6H_5)_2C(OH)COOC_2H_5$	$C_6H_5N(MgBr)_2$	$(C_6H_5)_2C(OH)CONHC_6H_5$	78.4	174-175	175 [4]
11				37.7	135-136	134-135

It should be noted that the application of organodimagnesium amine derivatives for the indicated purpose has not been described in the literature.

We conducted a reaction between $ArN(MgBr)_2$, where Ar = C_6H_5, o-$CH_3C_6H_4$ and β-$C_{10}H_7$, on the one hand and the esters of mono- and dibasic acids and their derivatives, on the other hand.

*In all the experiments, the yield of arylamide was calculated on the basis of the amine taken for the reaction.

Methods. Ethylmagnesium bromide was obtained from 0.05 mole of ethyl bromide and 0.05 mole of magnesium in 25 ml of ether. An ethereal solution of 0.025 mole of aromatic amines was added to the latter while it was being stirred. After evolution of ethane the reaction mass was heated on a water bath for 30 minutes. At the same time the organomagnesium amine derivative (ArNHMgBr) which was being formed reacted with ethylmagnesium bromide and N,N-bis-(bromomagnesium)-arylamine was obtained. At the end of the reaction the vigorous evolution of ethane changed to regular boiling of the ether.

A solution of 0.025 mole of the carboxylic acid ester in 10-20 ml of ether was added to an ethereal solution of 0.025 mole of N,N-bis-(bromomagnesium)-arylamine. The reaction mass was decomposed with 10% hydrochloric acid after having been heated for 30 minutes on the water bath and the arylamide which formed was isolated by the usual method.

The experimental results are presented in the table.

It is evident from the tabular data that the yield of arylamides based on the amount of amine taken for the reaction amounts to 7.15-98.7% of the theoretical.

The anilide of salicyclic acid which was obtained in a yield of 37.7% (Experiment 11) appears to be an exception. This is to be explained by the fact that the labile hydrogen of the salicylic ester phenol group decomposes the N,N,bis-(bromomagnesium)-arylamine, converting it into arylbromomagnesium amines.

The dibenzoyl derivatives of aromatic amines were obtained in excellent yields by the action of N,N-bis-(bromomagnesium)-arylamines on benzoyl chloride. The reaction proceeds according to the following scheme:

$$ArN(MgBr)_2 + 2C_6H_5COCl \longrightarrow ArN(COC_6H_5)_2 + MgBr_2 + MgCl_2.$$

Method. 0.05 mole of benzoyl chloride was added to 0.025 mole of N,N-bis-(bromomagnesium)-arylamine, obtained as indicated above. The reaction mass was heated for 1.5 hourson a water bath and then decomposed with 10% hydrochloric acid. The dibenzoyl amine derivative was isolated from the ethereal layer after elimination of the solvent.

Dibenzoyl-o-toluidine was obtained in a yield 91.1% of the theoretical. M.p. 109-110°. Literature data: 111-112° [5]. Dibenzoylaniline was obtained in a yield 74.2% of the theoretical. M.p. 160-161°. According to the literature data, dibenzoylaniline melts at 160-161° [6].

SUMMARY

1. The reaction of N,N-bis-(halomagnesium)-arylamines with esters and acid halides was studied. It was thereby established that N,N-bis-(halomagnesium)-arylamines react like organodimagnesium compounds.

2. It was established that the reaction between esters and N,N-bis-(halomagnesium)-arylamines has a number of advantages in comparison with arylhalomagnesiumamines and can be recommended for the synthesis of arylamines of mono- and dibasic acids, and of halogen-, hydroxy- and α,β-unsaturated acids.

3. The example of the reaction of N,N-bis-(bromomagnesium)-phenyl- and o-tolylamines with benzoylchloride demonstrated the possibility of applying this reaction for the synthesis of dibenzoyl derivatives of aromatic amines.

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STERIC HINDRANCE AND PROPERTIES OF CERTAIN ARYLAMINONAPHTHOQUINONES

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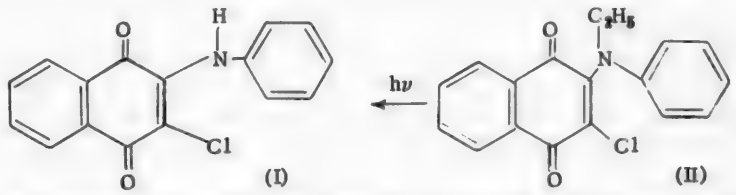
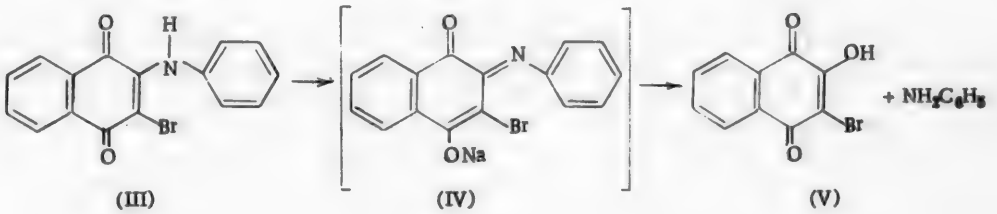
It was recently shown by us that 2-anilino-3-chloronaphthoquinone-1,4 ("the ethyl-less derivative") (I) and 2-N-ethylanilino-3-chloronaphthoquinone ("the ethyl derivative") (II) differ significantly from each other [1]. This difference in the ethyl derivative (II) in comparison with compound (I) is manifested: 1) in the markedly changed color and displacement toward the short waves of the absorption maximum; 2) in the lower melting point; 3) in the considerably greater solubility in organic solvents; 4) in the lower stability toward alkalis and 5) in the increased sensitivity of solutions to the action of light (see the table).



Such a marked difference in the properties of substances (I) and (II) was explained by the peculiarities in the chemical structure of their molecules; specifically, in the presence of steric hindrance in the ethyl derivative. The study of stereochemical models of compounds (I) and (II) demonstrated that the phenyl radical in the ethyl derivative (II), thanks to the presence of a halogen atom in the ortho position, is displaced from the plane occupied by it in the ethyl-less derivative (I) and has limited possibility of rotation.

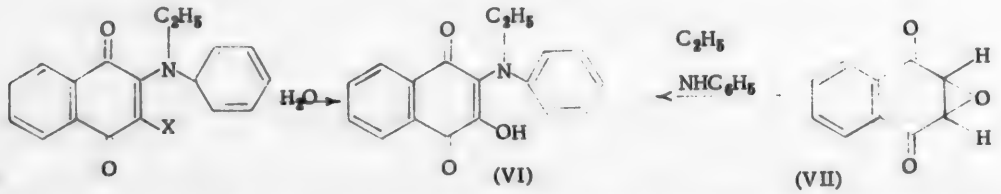
The behavior of the ethyl derivative in sunlight turned out to be particularly interesting. Even after brief irradiation the violet color of an alcohol solution is converted into red and then into orange. A red crystalline product was obtained from the solution in a yield of ~60% after it had been concentrated, and turned out to be the "ethyl-less derivative" (I). A characteristic photochemical reaction consequently proceeds during exposure to sunlight in which cleavage of the ethyl group from the nitrogen atom and conversion of the initial substance (II) into 2-anilino-3-chloronaphthoquinone (I) takes place.

The behavior of substances (I) and (II) toward alcoholic alkali is no less interesting. Miller in Markovnikov's laboratory [2] had already observed that 2-anilino-3-bromonaphthoquinone-1,4 (III) is readily hydrolyzed by alcoholic alkali, with the formation of 2-hydroxy-3-bromonaphthoquinone-1,4 (V). Evidently, an orthoquinoid tautomer with an arylimine bond (IV) appears here as in intermediate product. The instantaneous conversion of the orange color of a solution of the substance in alcohol into dark violet during addition of alkali argues in favor of this. After a short time the solution becomes brown and the hydroxy product (V) precipitates from it on acidification:



The chloro derivative (I) acts in exactly the same way as the bromo derivative. It is smoothly hydrolyzed into 2-hydroxy-3-chloronaphthoquinone-1,4.

Such tautomerism is naturally impossible in the 2-N-ethylanilino-3-chloronaphthoquinone (II) and hydrolytic cleavage of the arylamino group does not take place. However, the presence of steric hindrance in the ethyl derivative influences the properties of the halogen atom. The latter acts as though it were aliphatic in its character and is readily replaced by the hydroxyl group, yielding a new derivative, the 1,4-naphthoquinone (VI). The substance with the structure (VI) was synthesized from 2,3-hydroxy-,4-naphthoquinone (VII) [4] and ethylaniline; it turned out to be identical with the hydrolysis product of the ethyl derivative.



It was of interest to consider the properties of the related compounds in which the steric hindrance should be approximately the same as in the 2-N-ethylanilino-3-chloroderivative.

In connection with this the behavior of the 2-N-ethylanilino-3-bromo derivative (VIII) and also of the acetylated compounds (IX, X) during exposure to sunlight and the reactivity of the halogen atom werestudied.

The bromo derivative (VIII), 2-N-ethylanilino-3-bromonaphthoquinone-1,4 was prepared in a yield of 80-85% of the theoretical by boiling an alcoholic solution of 2,3-dibromonaphthoquinone-1,4 with ethylaniline. This product, which crystallized well from alcohol, had a dark blue color and m.p. 99-100°. It was somewhat more difficultly soluble than its chlorine analog in organic solvents (in alcohol, ether, benzene and others), however, the solubility of the substance was considerably greater than that of the ethyl-less derivative (III). The bromo derivative (VIII) was very similar to the chlorine analog (II) in its properties. Thus, the bromine atom in its molecule was also distinguished by a great lability, and during reaction with alcoholic alkali was replaced readily, almost quantitatively, by the hydroxyl group. Even in the cold the violet alcoholic solution of substance (VIII) rapidly became brown during the addition of NaOH solution. A dark-blue precipitate settled out during the acidification of such a solution with hydrochloric acid, and consisted of the above-mentioned 2-N-ethylanilino-3-hydroxynaphthoquinone-1,4 (VI).

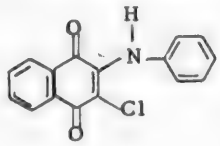
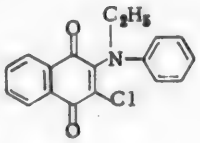
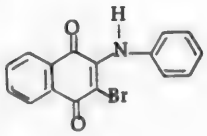
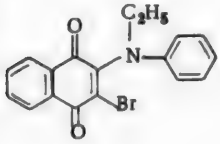
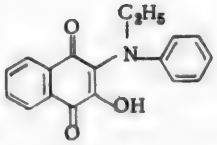
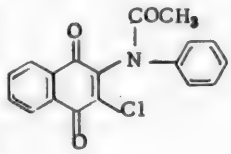
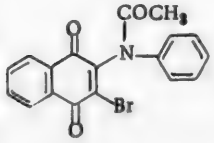
During the exposure of an alcoholic solution of 2-N-ethylanilino-3-bromonaphthoquinone-1,4, the cleavage of the ethyl group and formation of 2-anilino-3-bromonaphthoquinone (III) occurs:

Consequently, both for the chloro derivative (II) and for the bromine analog (VIII) with a noncoplanar structure of the molecule, there takes place this peculiar photochemical reaction with splitting off of the $-C_2H_5$ group and formation of a substance with greater possibilities of planar arrangement of groups.

In order to elucidate the problem of the mechanism of this peculiar reaction it was in the first place necessary to establish whether or not atmospheric oxygen participated in the process of splitting off the ethyl group. With this object the exposure of solutions of 2-N-ethylanilino-3-bromonaphthoquinone (VIII) was conducted parallelly in two flasks; one was exposed to air and air was excluded from the other by a stream of gaseous carbon dioxide. Approximately the same quantity of 2-anilino-3-bromonaphthoquinone (yield ~40%) was isolated from both solutions after a 30-hour exposure. This argued in favor of the assumption that the conversion of the ethylated product into the ethyl-less derivative proceeded without participation of atmospheric oxygen, and consisted of a process involving the cleavage of the ethyl group in which, possibly reduction occurs more rapidly than oxidation*.

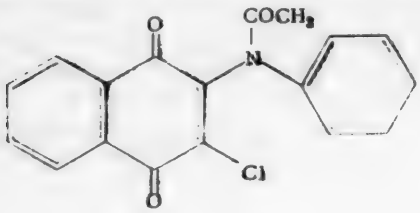
*The mechanism of this characteristic photoreaction should be studied in still greater detail.

Properties of Naphthoquinonephenylamines, Unsubstituted and Substituted at the Nitrogen Atom

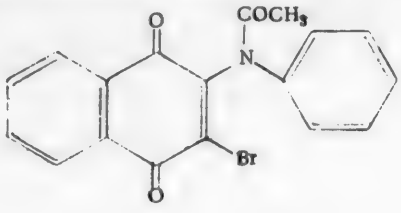
Experiment No.	Formula	Color of the crystals	Color of an alcoholic solution	Melting point (in °)	Solubility in benzene	$E_{1/2}$* (in volts relative to a calomel electrode	Reactivity of the halogen atom
1		Red	Orange	208-210	Very difficultly soluble	−0.245	Inert
2		Reddish Brown	Violet	94- 95	Very excellently soluble	−0.152	Reactive
3		Red	Orange	194-195	Difficultly soluble	−0.245	Inert
4		Dark Violet	Violet	99-100	Quite soluble	−0.150	Reactive
5		Blue	Blue	151-152	Quite soluble	−0.298	—
6		Yellow	Bright Orange	134-135	Quite soluble	−0.108	Reactive (replaced by the amino group)
7		Dark Yellow	Yellow	142-143	Quite soluble	−0.105	Reactive (replaced by the amino group)

* The polarographic investigations were conducted in a buffer solution of 0.1 N CH_3COONa and 0.1 N CH_3COOH in 75% alcohol.

The properties of acetyl derivatives were further studied and specifically, the properties of 2-N-acetylanilino--3-chloronaphthoquinone (IX) [5] and 2-N-acetylanilino-3-bromonaphthoquinone (X):



(IX)



(X)

The latter substance, not described in the literature, was prepared by the acetylation of the bromo derivative (III) with acetic anhydride in the presence of concentrated sulfuric acid.

As was demonstrated by stereochemical models, the space occupied by the $COCH_3$ group is approximately equal to that occupied by the C_2H_5 group. In connection with this, the steric hindrance due to the acetyl group in compounds (IX) and (X) should be approximately equal to that which is due to the ethyl group in compounds (II, and VIII).

Actually, the acetyl derivatives, similarly to the ethyl derivatives, have low melting points and differ considerably in their greater solubility in organic solvents from the unsubstituted products. The chlorine atom of compound (IX) is known to have considerable reactivity (for example, it is readily exchanged for the amino group [5]), in contrast to the free compound (I). Like the ethyl derivatives, the acetyl products have low half-wave potentials, (see the table). However, the acetyl products (IX, X) are markedly different in the color of their crystals and solutions from those of the ethyl products (II and VIII) – they are yellow colored.

Exposure of solutions of these substances to sunlight did not evoke appreciable visible change in their color (the orange color of the solution only became slightly brighter) and it appeared externally that the substances had not changed. It turned out, actually that the substances had undergone profound change. After distilling off the solvent we succeeded in isolating a small quantity of the corresponding ethyl-less derivatives (I) and (II). Among the decomposition products of the acetyl derivatives, the presence of ammonia and halogen derivatives which exhibited the halide ion reactions were detected qualitatively.

The investigation thus demonstrated that, with the acetyl products, in connection with the presence of steric hindrance, a characteristic cleavage takes place during exposure to sunlight which under equal conditions proceeds more profoundly than with the ethyl derivatives. This circumstance and the noticeable difference in color in comparison with the ethyl derivatives (II) and (VIII) (see the table) may be associated with the fact that in the acetyl derivatives the unshared electron pair at the nitrogen atom is displaced in the direction of the carbonyl of the acetyl group and has less possibility of interaction with the quinoid ring.*

Comparison of the properties of the N-ethyl- and N-acetyl derivatives argues in favor of the assumption that unshared electron pairs, present in our case on the nitrogen and halogen atoms, play an important role in the complex interrelationships of groups and atoms caused by the presence of steric hindrance.

The stability of the ethyl-less derivative (I) during exposure, appears, however, to be relative. A gradual change in the ethyl-less derivative is also observed under the influence of sunlight, but it takes place to a considerably smaller extent than in the case of exposure of the N-ethyl derivative. The light sensitivity of 2-anilino--3-chloronaphthoquinone has, however, other causes and is apparently associated with the conversion of the paraquinone into orthoquinones (IV).

EXPERIMENTAL

Preparation of 2-N-Ethylanilino-3-bromonaphthoquinone-1,4

1 g (0.003 mole) of 2,3-dibromonaphthoquinone [2] which was dissolved in 220 ml of ethyl alcohol by heating on a water bath, was placed in a round bottom flask supplied with a reflux condenser. A solution of 1 g of freshly prepared ethylaniline in 5 ml of alcohol was poured into the hot solution.

* Compare the observations of Levkoev, Sveshnikov and Barvin on the role of acyl-amino groups in the color of thiocarbocyanines with steric hindrance [6].

The mixture was heated on a water bath for 24 hours. The orange solution gradually became violet. After the dark violet solution obtained had been cooled, it was filtered off from the insignificant quantity of unreacted dibromonaphthoquinone. The alcohol was completely driven off and 15 ml of hydrochloric acid (1:4) was poured into the dark violet colored liquid which remained, to remove unreacted ethylaniline.

100 ml of ethyl ether was added to the mixture to extract the violet product. The ether was driven off and the resinous mass which remained was dissolved by heating in 50 ml of ethyl alcohol; on cooling, a precipitate settled out in the form of violet crystals (consisting under the microscope of green translucent rhombohedra). The precipitate was filtered off and dried. The yield of product was 1.0 g (87%) with a m.p. of 98-99°. The melting point did not change after recrystallization. The product was readily soluble in alcohol, benzene, ether and chloroform, giving a violet color.

4.390 mg sub.: 0.157 ml N_2 (23°, 724 mm). 0.0733 g sub.: 0.0383 g AgBr (Carius). Found %: N 4.09, Br 22.23. $C_{18}H_{14}O_2NBr$. Calculated %: N 3.93; Br 22.26.

Hydrolysis of 2-N-Ethylanilino-3-bromo- and 3-Chloronaphthoquinone-1,4

0.36 g (0.001 mole) of 2-N-ethylanilino-3-bromonaphthoquinone was dissolved in 20 ml of alcohol. 1 ml of 30% NaOH solution was added to the violet solution. The solution rapidly began to change color and after 20-30 minutes acquired a brown color. After 30 minutes the solution was acidified with 10 ml of a 2N HCl solution, whereupon the color of the solution changed to blue and a crystalline blue precipitate settled out. The reaction mass was diluted with 20 ml more of water and left for 2 hours until the precipitate had entirely settled out. After this, the precipitate was filtered off, washed free of acid with water and dried. The weight of the precipitate was 0.27 g (93%), m.p. 150-151°.

When mixed with 2-N-ethylanilino-3-hydroxynaphthoquinone-1,4, the hydrolysis product obtained did not depress the melting point.

The hydrolysis of 1-N-ethylanilino-3-chloronaphthoquinone-1,4* was conducted analogously. In this case 0.26 g (90%) of a blue crystalline product with a m.p. of 150-151°, which was identical with 2-N-ethylanilino-3-hydroxynaphthoquinone-1,4 was isolated from 0.32 g (0.001 mole).

Preparation of 2-N-Ethylanilino-3-Hydroxynaphthoquinone-1,4

0.88 g (0.005 mole) of 2,3-dihydroxynaphthoquinone-1,4 [4] was heated to boiling with 5 ml of ethyl alcohol. 0.54 g of ethylaniline was added to the solution. The color of the solution became dark violet. After having been boiled for 9 hours the solution was cooled, the precipitate which settled out was filtered off and washed with dilute hydrochloric acid, water and with alcohol. The weight of the precipitate was 0.7 g and the m.p. 148°. The precipitate was recrystallized from 10 ml of alcohol. The weight was 0.5 g (34%), m.p. 151-152°, which did not change after recrystallization. The product consisted of blue needle like crystals. It was very readily soluble in alcohol and in glacial acetic acid. It dissolved in alkalis, yielding a brown color. It dissolved in concentrated H_2SO_4, giving a rose color. It separated unchanged when the solution was diluted.

4.630 mg sub.: 0.194 ml N_2 (18°, 740 mm). 6.170 mg sub.: 0.267 ml N_2 (18°, 747 mm). Found%: N 4.79, 4.95. $C_{18}H_{15}O_3N$. Calculated %: N 4.77.

Behavior of 2-N-Ethylanilino-3-chloro- and 2-N-Ethylanilino-3-bromonaphthoquinone on Illumination with Sunlight**

1.50 mg of 2-N-ethylanilino-3-chloronaphthoquinone was dissolved in 100 ml of ethyl alcohol in a quartz flask. The flask with the violet solution (reddish tinge) was placed in sunlight for approximately 60 hours. Even after the first 20 hours of exposure there was a noticeable change of the violet color into reddish, which lost color and became orange with a brown tint. After the conclusion of the illumination there was a rather distinctly perceptible isonitrile odor in the alcoholic solution (there was no acetaldehyde odor). The alcohol was driven off and

* 2-N-Ethylanilino-3-chloronaphthoquinone-1,4 was prepared according to the data of reference [3]. Nothing was stated concerning the yield of product in the latter. The substance was obtained in small yields (around 10-20%) in our experiment. The reaction proceeded considerably more slowly than in the case of the bromo derivative.

** Both substances in quantities of 50 mg and 57 mg respectively were dissolved in 100 ml of alcohol and were subjected in closed quartz flasks to 130 hours exposure to a quartz lamp (1 kW at a distance of 60 cm). After this period the solutions became light brown with a brown tint. 10 mg of the red chloride with a m.p. of 196-200° and 8 mg of impure bromide with a m.p. of 166-170° could be isolated from the solutions.

After evaporation of the mother liquors a resinous brownish-yellow residue remained. The odor of acetaldehyde was distinctly perceptible in the solution. In the given case, apparently, a considerable portion of the ethyl-less products which were formed was more profoundly decomposed in the exposure process than during exposure to direct sunlight.

the volume reduced to 5 ml, and the brownish-red solution was left to cool. The fine red crystalline precipitate which settled out was washed with a small quantity of alcohol and dried. The weight of the precipitate was 16 mg, and the m.p., 205-207° (208-210° according to the literature data). About 3 mg more of the red product (impure) was isolated from the mother liquor.

The crystalline product was identified as 2-anilino-3-chloronaphthoquinone (a mixed sample did not cause depression of the melting point; polarograms of alcohol solutions of the synthetic product and the product of the photochemical cleavage were identical).

2. The experiment with 2-N-ethylanilino-3-bromonaphthoquinone was conducted under the same conditions as with the chlorine analog. 57 mg of the product under investigation was dissolved in 100 ml of alcohol in a quartz flask. Change of the violet color into red proceeded even after 20 hours of exposure. During further exposure the color of the solution gradually became paler, and at the end of the exposure became brownish-orange (somewhat darker than for the chlorine analog). The solvent was then driven off to a volume of 3 ml. A red crystalline product precipitated on cooling. The latter was filtered off, washed with alcohol and dried. The weight of the product was 17 mg, m.p. 189-191°. A mixed sample with 2-anilino-3-bromonaphthoquinone had a m.p. of 190-191°, i.e., caused no melting point depression.

In a control experiment where the solution was in a carbon dioxide atmosphere, the results were analogous. 57 mg of 2-N-ethylanilino-3-bromonaphthoquinone-1,4 was taken for the exposure and 16 mg of 2-anilino-3-bromonaphthoquinone with a m.p. of 187-190° was obtained. During a 16 hour exposure during which the violet color of the solution changed into red, 28 mg of a red crystalline product with a m.p. of 176-177°, after recrystallization — m.p. 190-192° — was isolated.

Preparation of the 2-N-Acetylanilino-3-chloronaphthoquinone

The acetyl derivative was obtained by the acetylation of 2-anilino-3-chloronaphthoquinone with acetic anhydride with the addition of concentrated sulfuric acid [5]. It was a yellow crystalline product with a m.p. of 134°.

Preparation of 2-N-Acetylanilino-3-bromonaphthoquinone-1,4

The product was obtained by the acetylation of 2-anilino-3-bromonaphthoquinone-1,4 with acetic anhydride (in the presence of a small quantity of strong H_2SO_4). 0.98 g (0.003 mole) of 2-anilino-3-bromonaphthoquinone-1,4 was taken for the experiment. 0.53 g (50%) of the acetyl derivative with a m.p. of 140-141° was obtained. The m.p. after recrystallization was 142-143°. The substance was readily soluble in alcohol, benzene, glacial acetic acid, chloroform, in contrast to the starting material which was difficultly soluble in these solvents.

6.570 mg sub.: 0.196 ml N_2 (22°, 735 ml). Found %: N 3.97. $C_{18}H_{12}O_3NBr$. Calculated %: N 3.78.

Behavior of 2-N-Acetylanilino-3-chloronaphthoquinone (IX) and 2-N-Acetylanilino-3-bromonaphthoquinone (X) in Sunlight

1. 52 mg of 2-N-acetylanilino-3-chloronaphthoquinone, dissolved in 100 ml of alcohol (orange solution), was subjected to exposure for 60 hours. Even in the first 10-15 hours the color of the solution became lighter; thereafter, it remained unchanged visually.

The alcohol was driven off until the volume was reduced to 3 ml. The dark orange solution was cooled. $\sim$ 3 mg of a red crystalline product with a m.p. of 204-205° precipitated, which appeared to be 2-anilino-3-chloronaphthoquinone. After concentrating the mother liquor a vitreous dark yellow mass remained from which the individual substances could not be isolated.

The presence of ammonium salts and Cl ions was detected qualitatively.

2. 59 mg 2-N-acetylanilino-3-bromonaphthoquinone, dissolved in 100 ml of alcohol, was subjected to exposure to light in an analogous manner. The solution was light orange and its color was not appreciably changed in the exposure process. After distilling off the solvent to a volume of 3 ml, 1.2 mg of 2-anilino-3-bromonaphthoquinone with a m.p. of 180-183° (impure) was isolated from the cooled solution. The filtrate was concentrated further to a volume of 1 ml and again cooled. Only a very insignificant quantity of the bromoanilide precipitated as a result of this. No other products could be isolated.

A strong odor of ammonia was perceived during the alkalinization of the aqueous residue after ether extraction and the presence of the Br ion was detected qualitatively.

SUMMARY

1. The behavior under the action of light of the N-ethylated and N-acetylated derivatives of 2-anilino-3-halonaphthoquinone-1,4 was studied. The ethylated and acetylated products split off the ethyl or acetyl group during

the action of sunlight and are converted into the unsubstituted products. The reactivity of the halogen atom in position 3 was also characteristically increased in the ethylated and acetylated compounds.

2. The photochemical cleavage of groups at the nitrogen atom and also the increased reactivity of the halogen atoms in the ethylated and acetylated products were explained by the presence in their molecules of steric hindrance due to the adjacent positions of the halogen atom and the N-ethylaniline radical in the quinoid ring of naphthoquinone.

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* See Consultants Bureau Translation, page 997.

SYNTHESIS AND REACTIONS OF 3,4-DIKETONES OF THE TETRAHYDROFURAN SERIES

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The 3,4-diketones of the tetrahydrofuran series constitute a very interesting but slightly studied class of compounds. There are no good general methods for the synthesis of these diketones, and only a few of these compounds have been described.

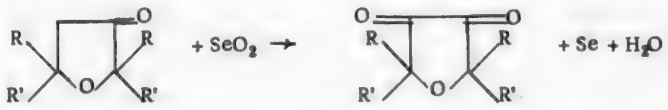
Dupont [1] established in 1913 that during the distillation of 4-nitro-2,2,5,5-tetramethyltetrahydrofuranone-3, along with other reaction products there is formed "a red liquid, boiling around 170°. Left in the moist air it is converted into a white crystalline mass, which melts around 80° after drying and is converted into a red liquid". Dupont deduced from his analytical data that the white crystalline substance was apparently the dihydrate of 2,2,5,5-tetramethyltetrahydrofurandione-3,4. In 1949 this same author [2] showed that during the dehydration of 2,5-dimethylhexandiol-2,5-dione-3,4 with the aid of phosphorus pentoxide, 2,2,5,5-tetramethyltetrahydrofurandione-3,4 is formed, which was characterized by preparing the dioxime, the mono-2,4-dinitrophenylhydrazone, and the quinoxaline from it.

In 1930 T. I. Temnikova and P. A. Tikhomolov [3] established that 2,2,5,5-tetra-o-tolyltetrahydrofurandione-3,4 is formed in a yield of 42% of the theoretical by the oxidation of tetra-o-tolylbutynediol with chromic anhydride in acetic acid.

It was later shown [4] that under analogous conditions tetraphenylbutynediol is converted into 2,2,5,5-tetraphenyltetrahydrofurandione-3,4 (yield 51%). Both these diketones have a bright raspberry color. They were characterized by preparing the monophenylhydrazone, the monooxime and the quinoxaline.

It is well known that α-diketones, α-dialdehydes and α-ketoaldehydes are obtained in excellent yields during the selenium dioxide oxidation of ketones or aldehydes containing a methyl or methylene group in the α-position to the carbonyl group [5]. However, this method, well worked out for the synthesis of α-diketones of the aliphatic, aliphatic-aromatic and alicyclic series, has not been employed for the synthesis of α-diketones of a heterocyclic series.*

The oxidation with selenium dioxide of two ketones of the tetrahydrofuran series — 2,2,5,5-tetramethyltetrahydrofuranone-3 and 2,5-dimethyl-2,5-diethyl-tetrahydrofuranone-3 — was studied in the present work. These ketones were chosen because there is only one methylene group close to the carbonyl group in them and, consequently, their oxidation should lead to only one reaction product:



1) $R = R' = CH_3$
2) $R = CH_3$; $R' = C_2H_5$

We established that during the oxidation of 2,2,5,5-tetramethyltetrahydrofuranone-3 and 2,5-dimethyl-2,5-diethyltetrahydrofuranone-3 with selenium dioxide in dioxane at 100° for 10 hours, 2,2,5,5-tetramethyltetrahydrofurandione-3,4 (yield 83.5% of the theoretical) and 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 (yield 86.5% of the theoretical) were respectively obtained.

2,2,5,5-Tetramethyltetrahydrofurandione-3,4 consists of a crystalline substance (m.p. 54-56°), bright raspberry colored, which is converted into a white dihydrate (m.p. 74-75°) in air. 2,5-Dimethyl-2,5-diethyltetrahydrofurandione-3,4 is a bright raspberry colored liquid with a b.p. of 93-95° (15 mm), which does not add water in air, but which is hydrated to give colorless solutions when dissolved in water.

* In Richet's work [6], "Halogen Derivatives of 2,2,5,5-tetramethyltetrahydrofuranone-3" it is mentioned that 2,2,5,5-tetramethyltetrahydrofurandione-3,4 is formed by the oxidation of 2,2,5,5-tetramethyltetrahydrofuranone-3 with selenium dioxide. However, neither the conditions under which the experiment was conducted, nor the yields of reaction products, nor the constants of the reaction are set forth in the work.

In the present work a suitable preparative method was thus worked out for the preparation of diketones of the tetrahydrofuran series in which there are tertiary carbon atoms in positions 2 and 5, and ketone groups in positions 3 and 4.

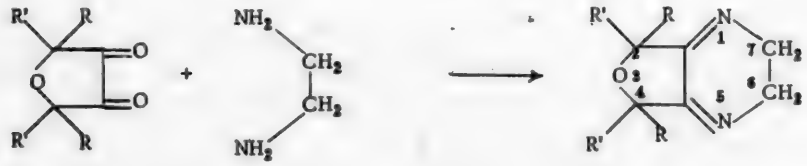
The diketones prepared by us gave all the characteristic reactions for α-diketones. Thus, the dioxime (yield 84%) of 2,2,5,5-tetramethyltetrahydrofurandione-3,4 was prepared by the action on the latter of hydroxylamine hydrochloride in water-alcohol solution.

The dioxime of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 (yield 50%) was also obtained.

Like all α-diketones, α-dialdehydes and α-ketoaldehydes, the diketones obtained by us readily react with o-phenylenediamine to give quinoxalines – 2,2,4,4-tetramethyltetrahydrofuro-(3,4)-quinoxaline (yield 85%) and 2,4-dimethyl-2,4-diethyltetrahydrofuro-(3,4)-quinoxaline (yield 86%):

1) R = R' = CH_3; 2) R = CH_3; R' = C_2H_5

The diketones prepared by us reacted vigorously with ethylenediamine to form dihydropyrazines.



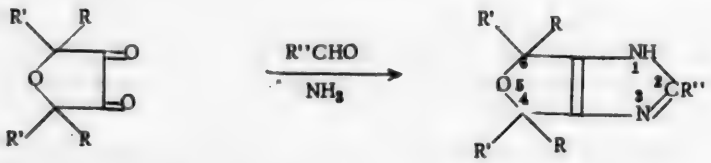
1) R = R' = CH_3; 2) R = CH_3; R' = C_2H_5

2,2,4,4-Tetramethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine was prepared in a yield of 81% of the theoretical and 2,4-dimethyl-2,4-diethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine – in a yield of 78% of the theoretical.

Radzishevsky [7] established as early as 1882 that the reaction of α-dialdehydes or α-diketones with ammonia and aldehydes can surve as an excellent method of synthesis for various imidazoles.

The diketones of the tetrahydrofuran series prepared by us also give imidazoles in excellent yields on reaction with aldehydes and ammonia. 4,4,6,6-Tetramethyltetrahydrofuro-(3,4)-imidazole (yield 70%) and 2-phenyl-4,4,6,6-tetramethyltetrahydrofuro-(3,4)-imidazole (yield 82%) were respectively prepared by the reaction of 2,2,5,5-tetramethyltetrahydrofurandione-3,4 with hexamethylene-tetramine or benzaldehyde and ammonia.

2,5-Dimethyl-2,5-diethyltetrahydrofurandione-3,4 reacts with hexamethylenetetramine and ammonia to give 4,6-dimethyl-4,6-diethyltetrahydrofuro-(3,4)-imidazole (yield 80%):



1) R = R' = CH_3; R'' = H; 2) R = R' = CH_3; R'' = C_6H_5; 3) R = CH_3; R' = C_2H_5; R'' = H

The 3,4-diketones of the tetrahydrofuran series can thus serve as convenient starting materials for the synthesis of condensed heterocyclic systems, the structure of which includes the tetrahydrofuran and the quinoxaline, dihydropyrazine or the imidazole rings.

EXPERIMENTAL

1. Synthesis of 3,4-Diketones of the Tetrahydrofuran Series

A. Preparation of 2,2,5,5-Tetramethyltetrahydrofurandione-3,4. A solution of 14.2 g (0.13 mole) of selenium dioxide in 200 ml of moist dioxane was placed in a half liter three-necked flask supplied with a mechanical stirrer with a mercury seal, a dropping funnel and a reflux condenser. The solution was heated to boiling and 14.2 g (0.1 mole) of 2,2,5,5-tetramethyltetrahydrofuranone-3* was added dropwise. The solution was boiled and stirred for 10 hours. The selenium which precipitated was filtered off and the dioxane was distilled off from the solution. In all 8.5 g of selenium (94.5% of the selenium dioxide introduced) was isolated. The residue was dissolved in 200 ml of ether, neutralized with a saturated solution of sodium bicarbonate and washed with water. After driving off the ether from the ethereal solution which had been dried with roasted sodium sulfate, the residue was vacuum distilled; b.p. 85-86.5° (30 mm). The yield was 13 g (83.5%).

2,2,5,5-Tetramethyltetrahydrofurandione-3,4 consisted of bright raspberry colored crystals; m.p. (after sublimation in a sublimator in the presence of phosphorus pentoxide) 54-56°; b.p. 85-85.5° (30 mm); quite soluble in ether and isooctane.

2,2,5,5-Tetramethyltetrahydrofurandione-3,4 rapidly absorbs moisture in air and is converted into the white dihydrate with m.p. of 74-75° (after twofold recrystallization from water).

The dihydrate loses water on heating and is converted into a raspberry colored liquid. The white crystals of the dihydrate give a raspberry coloration to solutions in ether, alcohol and petroleum ether.

Found %: C 50.42, 50.37; H 8.59, 8.48. $C_8H_{12}O_3 \cdot 2H_2O$. Calculated %: C 49.98; H 8.99.

Literature data for 2,2,5,5-tetramethyltetrahydrofurandione-3,4: red liquid, b.p. 170°; m.p. of the white dihydrate around 80° [1].

B. Preparation of 2,5-Dimethyl-2,5-diethyltetrahydrofurandione-3,4. 15 g (0.088 mole) of 2,5-dimethyl-2,5-diethyltetrahydrofuranone-3** was oxidized with 15 g (0.136 mole) of selenium dioxide, as in the preceding experiment. After twofold vacuum distillation, 14 g (86.5%) of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 was obtained: b.p. 93-95° (15 mm); m.p. −12.2 to −11.8°; n_D^{20} 1.4422; d_4^{20} 1.0062; MR_D 48.48; calc. 47.85.
Found %: C 65.41, 65.63; H 8.98, 8.81. $C_{10}H_{16}O_3$. Calculated %: C 65.19; H 8.75.
2,5-Dimethyl-2,5-diethyltetrahydrofurandione-3,4 consisted of a bright raspberry colored liquid, quite soluble in alcohol, ether, dioxane and isooctane; 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 yielded colorless solutions when dissolved in water.

2,5-Dimethyl-2,5-diethyltetrahydrofurandione-3,4 had not been described in the literature.

2. Preparation of the Dioximes of 3,4-Diketones of the Tetrahydrofuran Series

A. The Dioxime of 2,2,5,5-Tetramethyltetrahydrofurandione-3,4. 1.8 g (0.36 mole) of hydroxylamine hydrochloride was added to a solution, cooled to 0°, of 0.8 g (0.005 mole) of 2,2,5,5-tetramethyltetrahydrofurandione-3,4 in a mixture of 15 ml of water and 25 ml of ethyl alcohol, and a solution of 2.3 g of potassium hydroxide in 10 ml of water was then added. The reaction mixture was heated for 2 hours on a water bath and then cooled and saturated with solid carbon dioxide. The precipitate which formed was filtered off and recrystallized from absolute ethyl alcohol. 0.8 g (84%) of the dioxime of 2,2,5,5-tetramethyltetrahydrofurandione-3,4 was obtained which melted at 224-225° after repeated recrystallization.

Found %: N 15.12, 15.18. $C_8H_{14}O_3N_2$. Calculated %: N 15.06.

The literature data for the dioxime of 2,2,5,5-tetramethyltetrahydrofurandione-3,4: volatilizes without melting at 240° [1]; volatilizes without melting at 210° [2].

B. The Dioxime of 2,5-Dimethyl-2,5-diethyltetrahydrofurandione-3,4. The method was analogous to the preceding. The dioxime of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 was obtained from 1.8 g (0.01 mole) of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 and 3.64 g (0.052 mole) of hydroxylamine hydrochloride: m.p. 193° (after recrystallization from aqueous ethyl alcohol). The yield was 1 g (50%).

Found %: N 13.11, 12.97. $C_{10}H_{18}O_3N_2$. Calculated %: N 13.06.

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* 2,2,5,5-Tetramethyltetrahydrofuranone-3 was synthesized by simultaneous hydration and dehydration of 2,5-dimethylhexyne-3-diol-2,5 in the presence of mercuric sulfate [1]: b.p. 149-149.5° (762 mm); n_D^{20} 1.4202; d_4^{20} 0.9249; MR_D 38.91; calc. 38.69.

** 2,5-Dimethyl-2,5-diethyltetrahydrofuranone-3 was prepared by the simultaneous hydration and dehydration of 3,6-dimethyloctyne-4-diol-3,6 in the presence of mercuric sulfate: b.p. 90-91° (25 mm); n_D^{20} 1.4383; d_4^{20} 0.9319; MR_D 47.97; calc. 47.90.

The dioxime of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 had not been described in the literature.

3. Preparation of the Quinoxalines of 3,4-Diketones of the Tetrahydrofuran Series

A. Preparation of 2,2,4,4-Tetramethyltetrahydrofuro-(3,4)-quinoxaline. A mixture of 0.4 g (0.0025 mole) of 2,2,5,5-tetramethyltetrahydrofurandione-3,4 and 0.25 g (0.0023 mole) of o-phenylenediamine was heated in a test tube until it melted. After the yellow crystalline mass which formed on cooling had been recrystallized twice from alcohol, 0.4 g (85%) of 2,2,4,4-tetramethyltetrahydrofuro-(3,4)-quinoxaline with a m.p. of 101.5° was obtained.

Found %: N 12.43, 12.29. $C_{14}H_{16}ON_2$. Calculated %: N 12.27.

Literature data for 2,2,4,4-tetramethyltetrahydrofuro-(3,4)-quinoxaline [2]: m.p. 98-99°.

B. Preparation of 2,4-Dimethyl-2,4-diethyltetrahydrofuro-(3,4)-quinoxaline. A mixture of 0.9 g (0.005 mole) of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 and 0.5 g (0.0046 mole) of o-phenylenediamine was heated in a test tube for 10-15 minutes. After the dark crystalline mass which formed on cooling had been recrystallized twice from ethyl alcohol, 1 g (86%) of 2,4-dimethyl-2,4-diethyltetrahydrofuro-(3,4)-quinoxaline was obtained: m.p. 110-111.5°.

Found %: N 10.83, 10.69. $C_{10}H_{20}ON_2$. Calculated %: N 10.52.

2,4-Dimethyl-2,4-diethyltetrahydrofuro-(3,4)-quinoxaline had not been described in the literature.

4. Preparation of Dihydropyrazines from 3,4-Diketones of the Tetrahydrofuran Series

A. 2,2,4,4-Tetramethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine. 3.12 g (0.04 mole) of ethylenediamine monohydrate was added to 6.2 g (0.04 mole) of 2,2,5,5-tetramethyltetrahydrofurandione-3,4. The reaction was accompanied by strong evolution of heat and a change in the color from red to yellow. The reaction mass was diluted with ether and dried with roasted potash. After distilling off the ether and twofold vacuum distillation, 5.8 g (81%) of 2,2,4,4-tetramethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine was obtained: b.p. 75.5-75.7° (9 mm); n_D^{20} 1.4755; d_4^{20} 1.0029; MR_D 50.97; calc. 50.56.

Found %: N 15.23, 15.34. $C_{10}H_{16}ON_2$. Calculated %: N 15.54.

2,2,4,4-Tetramethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine had not been described in the literature.

B. 2,4-Dimethyl-2,4-diethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine. 4.6 g (78%) of 2,4-dimethyl-2,4-diethyltetrahydrofuro-(3,4)-6,7-dihydrofuran was obtained under the same conditions as in the preceding experiment from 5.9 g (0.032 mole) of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 and 2.51 g (0.032 mole) of ethylenediamine monohydrate after twofold vacuum distillation: m.p. 98-98.2° (6 mm); 101° (8 mm); n_D^{20} 1.4789; d_4^{20} 0.9881; MR_D 59.77; calc. 60.21.

Found %: N 13.58, 13.67. $C_{12}H_{20}ON_2$. Calculated %: N 13.46.

2,4-Dimethyl-2,4-diethyltetrahydrofuro-(3,4)-6,7-dihydropyrazine had not been described in the literature.

5. Preparation of Imidazoles from the 3,4-Diketones of the Tetrahydrofuran Series*

A. 4,4,6,6-Tetramethyltetrahydrofuro-(3,4)-imidazole. A mixture of 0.13 g (0.001 mole) of hexamethylenetetramine and 3 g of ammonium acetate was dissolved in 20 ml of glacial acetic acid and boiled for 1 hour with a reflux condenser. The reaction mixture was then poured out into 100 ml of water and saturated with ammonia while it was being cooled. The solution was repeatedly extracted with ether. After the ethereal extract had been dried with roasted potash and the ether driven off, 4,4,6,6-tetramethyltetrahydrofuro-(3,4)-imidazole was isolated.

0.6 g (70.0%) of 4,4,6,6-tetramethyltetrahydrofuro-(3,4)-imidazole with a m.p. of 288-289° was obtained after twofold recrystallization from pyridine.

Found %: N 16.79, 17.04. $C_9H_{14}ON_2$. Calculated %: N 16.84.

4,4,6,6-Tetramethyltetrahydrofuro-(3,4)-imidazole was soluble in water, alcohol, acetone and hot pyridine. It had not been described in the literature.

B. 2-Phenyl-4,4,6,6-tetramethyltetrahydrofuro-(3,4)-imidazole. A mixture of 1.6 g (0.01 mole) of 2,2,5,5-tetramethyltetrahydrofurandione-3,4, 1.06 g (0.01 mole) of benzaldehyde and 10 g of ammonium acetate was dissolved in 50 ml of glacial acetic acid and heated for 1 hour with a reflux condenser. The reaction mixture was poured out into 300 ml of water and filtered free of suspension through activated carbon. The transparent solution

* The imidazoles were prepared by the method described for the synthesis of imidazoles from benzene [8].

was saturated with ammonia while being cooled, after which a voluminous precipitate settled out which was dissolved in 10 ml of hot pyridine and precipitated with 10 ml of hot water. 2 g (82%) of 4,4,6,6-tetramethyl-2-phenyltetrahydrofuro-(3,4)-imidazole was obtained after twofold recrystallization from acetone: m.p. 253-254°.

Found %: N 11.46, 11.36. $C_{15}H_{18}ON_2$. Calculated %: N 11.56.

2-Phenyl-4,4,6,6-tetramethyltetrahydrofuro-(3,4)-imidazole was soluble in hot acetone, alcohol and pyridine and insoluble in water; it had not been described in the literature.

C. 4,6-Dimethyl-4,6-diethyltetrahydrofuro-(3,4)-imidazole. 4,6-Dimethyl-4,6-diethyltetrahydrofuro-(3,4)--imidazole was obtained from 1.84 g (0.01 mole) of 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 and 0.26 g (0.002 mole) of hexamethylenetetramine under conditions analogous to those for the preparation of 4,4,6,6-tetramethyltetrahydrofuro-(3,4)-imidazole: m.p. 193-194° (after twofold recrystallization from dichloroethane). The yield was 1.2 g (80%).

Found %: N 14.62, 14.17. $C_{11}H_{18}ON_2$. Calculated %: N 14.42.

4,6-Dimethyl-4,6-diethyltetrahydrofuro-(3,4)-imidazole was quite soluble in water, pyridine, acetone, carbon tetrachloride, chloroform and hot dichloroethane. It had not been described in the literature.

SUMMARY

1. The oxidation with selenium dioxide of ketones of the tetrahydrofuran series with tertiary carbon atoms in positions 2 and 5 can serve as a convenient preparative method of obtaining diketones in which carbonyl groups are located in positions 3 and 4. 2,2,5,5-Tetramethyltetrahydrofurandione-3,4 and 2,5-dimethyl-2,5-diethyltetrahydrofurandione-3,4 were prepared in respective yields of 83.5% and 86.5% of the theoretical.

2. The 3,4-diketones of the tetrahydrofuran series appear to be convenient starting materials for the synthesis of condensed heterocyclic systems, the structure of which includes the tetrahydrofuran, and the quinoxaline, dihydropyrazine or imidazole rings.

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DISCUSSION

RESPONSE TO THE ARTICLE OF G. V. TSITSISHVILI APROPOS OF THE WORK OF A. A. KALANDIYA ENTITLED "CALCULATION OF MOLECULAR VOLUMES OF INORGANIC COMPOUNDS OF THE $A_nB_mO_s$ TYPE"

A. A. Kalandiya

An article by G. V. Tsitsishvili [1] has been devoted to the critical analysis of my work [10], "Calculation of Molecular Volumes of Inorganic Compounds of the $A_nB_mO_s$ Type".

Tsitsishvili did everything possible to distort the basic approach of my work and reproaches me because in my article ". . . ": He has not taken into consideration Butlerov's theory of chemical structure". However, before having made a statement so inaccurate (as will be shown below), it would have been helpful if Tsitsishvili had stated that in all his works [3-9] on the so-important topic of the structure of compounds, not only was the Butlerov theory of chemical structure never considered, but there was an overall silence concerning the very existence of A. M. Butlerov's structural theory.

On the basis of the substance of the works of Tsitsishvili and also of his recent communication concerning my work [1], one is forced to conclude that Tsitsishvili was trying to create the impression that he is an opponent of the "theory of resonance", thereby distracting attention from his own methodologically defective Machist-idealistic concepts.

It is impossible to describe his expressions except with use of the "terminology of the resonance concept" which he supported at the All-Union Congress on the State of the Theory of Chemical Structure in Organic Chemistry [2].

Not to dwell on the other works of Tsitsishvili based on an idealistic conception of the question, I pass over to the critical review of my article [10]. It was certainly far from my thoughts that Tsitsishvili was incapable of understanding the point of my work in the form in which it was set forth. Tsitsishvili, in his recently published article, disorients the reader by incorrectly interpreting my basic positions.

For example, Tsitsishvili maintains that I had attempted to calculate the forces F_z, while actually I calculate the radius R_{z_i}. As is evident from a mere glance at my work [10], I was undertaking to provide a method for calculating the molecular volumes and not the forces F_z. Apart from this, and contrary to the assertions of Tsitsishvili, in my entire paper, all calculations were subordinated to the goal of determining the molecular volume; this requires the quantities $R_{z_1z_2z_3}$, i.e., the distances between the centers of the cation and anion, and not R_{z_1} as Tsitsishvili incorrectly indicates.

It should be noted that Tsitsishvili endeavors to maintain that I was calculating the influence of some sort of extraneous ions on the distance between the ions B_m^{z+} and O_s^{f-}, concerning which nothing whatever was said in my article.

For clarity I present in its entirety a quotation, containing the essence of Tsitsishvili's criticism of my work. Tsitsishvili writes: "There is practically no basis for the expression for the attractive forces (see Equation 1). The introduction of the constant coefficient A, which Kalandiya glorifies as the 'Madelung Constant', has no basis here at all. The constant coefficient in the energy of attraction is a function of the type of lattice in the solid; it is usually used for the electrostatic calculation of the lattice energy. Here Kalandiya attempts to calculate the reaction between m positive ions B and s negative ions O. It is nowhere shown that the attractive force, F_1, is actually proportional to z_3 and z_4. It is appropriate to point out that in the foregoing foggy text, it is almost impossible to comprehend

the significance of z_1, z_2, z_3, and z_4. For instance, Kalandiya writes that 'z_1 = the charge employed for the bond with element A.' One must ask – the value of what charge and, probably, employed, rather than occupied by, as the author writes:) • for the bonds of what ions (and not elements, as the author confuses it)?"

In the first place it should be noted that in my work the symbols z_1, z_2, z_3, and z_4 denote the charges of ions and covalent bonds of elements entering into a complex substance. For example: in sodium sulfate the bond between sodium and oxygen is ionic while the bond of sulfur with oxygen is slightly polar and ions are generally not formed via bonding of sulfur with oxygen. Many such examples could be adduced. On this basis and in order to avoid confusion, since this is generally understood, in my work I preferred to call the simple substance an element.

I wish to note the following in order to avoid incorrect interpretations: it is well known that the properties of chemical bonds of both diatomic and polyatomic moledules are identical and there is no basis to employ Coulomb's law for diatomic molecules only. In addition, both in diatomic and in polyatomic molecules each nucleus actually interacts not with point charges but with an electron cloud. The distribution of the density of this electron cloud changes markedly with changes in the distance between nuclei. In spite of this it is conventional to consider that the attractive force of two ions of opposite sign obeys Coulomb's law. This involves the assumption that the charges of the ions are concentrated at one point.

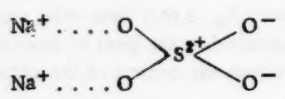
It should be noted here that in crystal lattices of binary compounds, for example, in sodium chloride, we have to do with a high-molecular complex compound $(NaCl)_n$. In spite of this it is well known that the attractive force of such crystalline compounds is calculated in the same way as for the simple binary compound. The energy of a mole of the crystalline substance is also calculated on the assumption that the force of interaction between each pair of ions obeys Coulomb's law, including Madelung's constant and not the Coulomb law of repulsion $\frac{B}{R^n}$.

I assumed in exactly the same way that the force of interaction between each pair of ions obeys Coulomb's law for polyatomic molecules. It was thereby taken into account that compound atoms basically influence each other through intermediate atoms and not directly. On the basis of this and the experimental data, the influence of the cation A_n^+ was taken into account for the attractive force F_1 between each pair of ions $B_mO_s^{f-}$ by means of the values z_3 and z_4; the proportionality of the influence of the cation A_n^+, contrary to the assertion of Tsitsishvili, was demonstrated on the basis of the results of 75 calculations and their comparison with the experimental data.

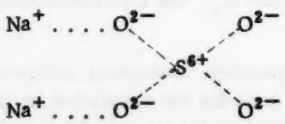
The constant coefficient A (Madelung's constant) introduced by me in the given case can also be considered necessary and justified. It is far from my thoughts, however, that my attempts to arrive at the calculation of the interatomic distances and molecular volumes were ideal and require no further development and precision.

To distract the attention of the reader from his own Machist-idealist errors which he has tolerated from the beginning of his career to the present time, Tsitsishvili maintains that the substance of my article amounts to an anti-Butlerov representation of the polystructure of molecules. However, as even the non-expert reader can readily see, my calculation of the molecular volume demonstrated that there is only one structural formula depicting the structure of the compound for each real compound; the simultaneous existence of other structures is thereby contradicted. Consequently, the results of my work are found to be in agreement with the teachings of A. M. Butlerov.

For example: Na_2SO_4 is either constructed according to the formula, composed of the ions Na^+, S^{2+}, and O^- with four covalent S – O bonds:



or according to the formula consisting of the ions Na^+, S^{6+} and O^{2-}:



• The Russian word originally used by Kalandiya has various synonyms, and might be translated as: occupied by, busied with, employed for. In the translation of the Kalandiya paper discussed here, Consultants Bureau chose the latter translation as most probably conveying the author's meaning.

Calculating the molecular volume for Na_2SO_4 according to my method [10] for the first structure, we find on the basis of the radii of the "mono-charged" ions that it is equal to 51.1 $Å^3$. It should actually be 53.2 $Å^3$, i.e., the error amounts to only 2.1 $Å^3$.

Assuming that Na_2SO_4 has the second structure, its molecular volume calculated according to my method on the basis of the ionic radii [11], is equal to 24.0 $Å^3$ instead of 53.2 $Å^3$, i.e., in this case the deviation is equal to 29.2 $Å^3$.

Thus, my calculation of the molecular volumes definitely demonstrates the probability of the first structure for Na_2SO_4.

A similar calculation was carried out by me for all the compounds which are set forth in Tables 3, 4, and 5 [10], but only the results obtained for one of the assumed structures for each distinct compound are set forth there. This again demonstrates that I adhere to the position that there is only one structural formula for each real compound which depicts the chemical structure of that compound. Consequently, contrary to the assertion of Tsitsishvili, the substance of my work is based not on a multi-structural, but on a monostructural theory.

As regards the sentence: "It must be assumed that the structure . . . . . in the second variant predominates over all the other structures expressed by the other variants in the state of mutual superposition of one over another."; [10], I recognize it to be erroneous and not proceeding from the results of my work and have so declared at the opportune time.

The attention of the reader should finally be directed to yet one more example of confusion created by Tsitsishvili. He writes: "It is impossible to understand why Kalandiya used K = 1.044 for $NaIO_4$ . . . . . Kalandiya states that he takes the coefficient of repulsion as 9. When he returns to the calculation of the $NaIO_4$ example, he assumes that it 'averages 7' ". Tsitsishvili further writes: "What is the average coefficient of repulsion, and, strictly speaking, on the basis of what data does Kalandiya take it to be 7 for $NaIO_4$, 7.3 for $NaBrO_4$, 8.3 for $CoWO_4$ and 9.3 for $PbMoO_4$?". In my work the number K is the ratio of the interatomic distances to the coordination number. In agreement with existing data [11], with a coordination number of 8 and a degree of repulsion of 7, as occurs in my case, K for $NaIO_4$ = 1.044. As is evident from the table presented on page 1638 of the article [10], inasmuch as $\underline{n}$ = 7 for oxygen, the average value of n for $CoWO_4$ is equal to 8.3

However, Tsitsishvili, without altering his method of ignoring entirely plain facts, in place of this quantity, $\underline{n}$, as an index of the order of the radical, calls the attention of the reader to an entirely baseless discussion of this very simple question, substituting for the above-mentioned ratio another symbol $\underline{n}$, found in the denominator, as a constant coefficient equal to 9.

Further, as is well known, in the equation $F = F_1 + F_2$ (3) [10], the right hand side of the equation is subject to partial integration. Avoiding this fact, Tsitsishvili talks of mechanical separation of the energy of interaction from the energy of attraction and repulsion as if it were my invention, saying: "the repulsion force mysteriously arises for Kalandiya at the instant of the mutual approach of the ions" [1]. By this Tsitsishvili assiduously attempts to conceal from the reader that what he calls the "very mysterious" Coulomb force is the action of the forces of attraction and repulsion between charged envelopes of ions (not the Coulomb force of repulsion), briefly designated in my work as

$$\frac{B}{R^{\underline{n}}}.$$

I hope that the examples which I have presented will warn the reader against the confusion created by Tsitsishvili.

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